

AN ABSTRACT OF THE THESIS OF

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The calcium concentration of seawater was measured for samples obtained from the recent Hawaii-Tahiti Shuttle Experiment. The complexometric titration used for the determination of calcium was shown to be free of interference from other alkaline earth elements at the 0.1% level of accuracy obtained. However ratios of interferant to calcium larger than those found in seawater did cause significant loss of accuracy.

The results of the investigation of the vertical distribution of calcium, in the equatorial region sampled, suggest that physical-circulation processes are more important than local-vertical production and dissolution of  $\text{CaCO}_3$  in creating the relative extrema observed. These samples from depths of 1000 m and less, have specific calcium values that inversely correlate with salinity and temperature. The lowest values of normalized ( to 35‰ salinity) calcium are found in the warm surface waters of highest salinity and appear to reflect biological depletion in the relatively unmixed waters of the central gyres. The higher specific calcium values are found in less saline waters from higher latitudes and reflect the higher "preformed" calcium values found in colder waters near the polar fronts. This "preformed" dependence can be seen in cross-sectional

comparison of calcium concentrations (normalized) across the equator. Here the calcium distribution has boundaries consistent with those between particular circulation features such as equatorial currents and possibly upwelled intermediate waters.

CALCIUM IN THE EQUATORIAL PACIFIC OCEAN

by

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## PREFACE

This thesis has been prepared in accordance with the most recent guidelines for thesis preparation in a manuscript format. As suggested in those guidelines an introductory chapter (1) is presented containing a review of the literature and a brief description of the results and conclusions of this work. Chapter 2 is essentially the experimental description presented in manuscript form and similarly, Chapter 3 is a manuscript containing the major oceanographic results and discussion of this work. The appendices presented at the end contain a theoretical treatment of the experimental technique and the data collected to evaluate the calcium distribution.

Due to the fact that the manuscripts are to be submitted to different journals, the exact form of the citations in the text may differ from chapter to chapter; however, they will be similar enough to make use of the common bibliography.

## CALCIUM IN THE EQUATORIAL PACIFIC OCEAN

### INTRODUCTION

The distribution of dissolved calcium in the world's oceans has been studied by many investigators in the last hundred years. Since the classic analyses of Dittmar (1884), who was probably the first to show greater calcium to chlorinity ratios at depth, a number of reports have been published further describing the vertical and horizontal variability in calcium concentration. Recently some initial effort has also been made to measure temporal variations in the calcium concentrations.

An understanding of the temporal variability is important in evaluating spatial distribution, but the temporal variability of calcium has not been well defined because of the difficulty of measuring its concentration in seawater and the lack of precise and accurate data. Billings, Bricker, MacKenzie and Brooks (1969) reported a range of about 17% in Ca/Cl values for samples taken from several depths at a single station over a period of nearly a year. Despite the documented care of the experimenters, the spectroscopic technique used was unreliable, thus the reported temporal variation is generally considered to be unlikely (Riley, 1975). A subsequent study of temporal variation using a more sensitive technique by Atwood, Froelich and Kinard (1973) found only about 7% variation in the Ca/Cl ratios over eleven months. Again, when the analytical precision was taken into account by these investigators, this variation was not considered to be significant. Data collected more recently by various investigators from approximately

the same oceanographic regions at different points of time rarely vary by more than 1 or 2%. These variations cannot, however, be considered as strictly temporal because of analytic offsets and the lack of intercalibration work. As a result, the temporal variation of calcium in the ocean has been considered to be probably no greater than the overall spatial variation of 1-2% in Ca/Cl generally shown for worldwide samples.

The bulk of the work on the spatial distribution of calcium in seawater has been done in the vertical dimension. The difference in calcium (relative to chlorinity or salinity) between surface waters and deep waters has been shown many times, and explanations, correlations with alkalinity, and some models have been given for this phenomenon. A summary of this work is probably best done chronologically.

Dittmar (1884) analyzed 77 samples from all over the world and found large differences in the calcium-chlorinity ratio between the surface and deep waters. He felt the analyses were subject to imprecision which exaggerated these differences (overall range in Ca/Cl of about 14%), but nonetheless he concluded on the basis of the original 77 samples and additional analyses of composite samples that deep waters were significantly richer in "lime".

Dittmar explained this phenomenon as the probable result of living organisms precipitating  $\text{CaCO}_3$  in the surface waters and the subsequent dissolution of the carbonate skeleton upon sinking. As support for this hypothesis, he was able to show a similar increase in alkalinity from surface to deep waters (normalized via salinity) and, in fact, used the mean difference in alkalinity to back calculate the change in calcium. The result was almost identical to that measured difference

between the composite surface and deep samples. While Dittmar felt that the closeness of this agreement was fortuitous, he did conclude that the difference in alkalinity was an indication of carbonate dissolution which would also account for the increases seen in calcium.

Thompson and Wright (1930) reported constant values for Ca/Cl ratios in the North Pacific within the precision of their measurements. Their samples were, however, limited to a small area and depth range. Wattenberg (1933), using more extensive data from the 1925-1927 "Meteor" cruises, concluded that the calcium concentration of seawater is made up of both constant and variable fractions. The constant or conservative fraction could be evaluated via chlorinity and the variable fraction would be equivalent to half the measured alkalinity,

$$[\text{Ca}^{2+}] \text{ (mM)} = 0.477 \times \text{Cl } \text{‰} + (\text{alkalinity}/2). \quad (1)$$

The study of Culkin and Cox (1966) on the ratios of the major cations to chlorinity based on 66 samples from around the world essentially confirmed Dittmar's findings. The overall range reported for Ca/Cl values was smaller than Dittmar's (about 1.5%), but they did measure a significant increase in values of Ca/Cl for samples from below 1100 m. They found a reversal of this trend in the Mediterranean Sea, but offered no explanation for this observation. Riley and Tongudai (1967) reported values for Ca/Cl almost identical in range and mean to those of Culkin and Cox for a similar selection of samples using a different analytical method.

Traganza and Szabo (1967) also supported the calcium-alkalinity relationship proposed earlier. Their data show decreases in both Ca/Cl

and specific alkalinity across (from seaward onto) the Great Bahama Bank, an area of very high salinity and known inorganic precipitation of  $\text{CaCO}_3$ . In addition, their summary of previous work in this region shows that the value of the chlorinity coefficient in equation (1) was generally found to be higher than that of Wattenberg (1933), although a fairly large range of values had been reported (overall range of 5.5% with standard deviations averaging  $\pm 0.8\%$ ).

Tsunogai, Nishimura and Nakaya reported both an analytical technique for the determination of calcium in seawater (1968a) and data on the calcium concentration in the Western North Pacific (1968b). Tsunogai et al. (1968b) concluded that not only does the value of Ca/Cl increase with depth, but it also varies horizontally at the surface. They found higher surface Ca/Cl values where water temperature and salinity were lower when comparing surface samples from adjacent regions of different temperature and salinity. Tsunogai and coworkers were among the first to suggest the ratio Ca/Cl might be used as a tracer of water masses.

Sagi (1969) collected data in the Western North Pacific extending south to the equator. He reported surface values lower than the lowest of Tsunogai et al. (1968b) (by about 1.8%) for Ca/Cl in the subtropic surface waters, but he too found greater values of Ca/Cl at depth although his deepest samples were from only 1500 m. He also noted the apparent inverse relation between Ca/Cl and surface water salinity and suggested that the very low values may have resulted from consumption in the "stagnant waters" of the Subtropics.

Values for Ca/Cl in the Indian and Antarctic Oceans were determined

by Tsunogai, Yamazaki and Nishimura (1971). While still demonstrating the relative enrichment of calcium in the deep waters of the Indian Ocean, the data showed much less difference between surface and deep waters in the Antarctic, which Tsunogai et al. concluded to be the result of active vertical mixing. Once again, the lowest Ca/Cl values were found in the warm and high salinity tropics and subtropics. These authors pointed out that calcium may follow, in the warm surface waters, the same tendencies as phosphate and nitrate, reflecting variations in biological activity. A reasonable correlation between surface values of phosphate and Ca/Cl values was obtained and suggested as evidence for biological utilization.

Tsunogai, Yamahata, Kudo and Saito (1973) published a major study on the horizontal and vertical distributions of calcium in the Pacific Ocean. Their analyses of over 1800 samples provided more evidence that the warm high salinity surface waters of the low and mid latitudes have the lowest Ca/Cl values and revealed that the North Pacific Deep Water has the highest values. Their overall range in Ca/Cl values was about 1.6%.

Tsunogai et al. (1973) attempted to relate chlorinity-normalized calcium with specific alkalinity using the stoichiometry of the  $\text{CaCO}_3$  precipitation - dissolution concept. However, their data showed anomalously high calcium values between 1 and 2 km for most of their north-south cross section of the Pacific as well as high calcium at nearly all depths north of 35-40°N. They hypothesized an undiscovered calcium input to these regions possibly related to the ion exchange of silicate materials in the water column.

Horibe, Endo and Tsubota (1974) found that salinity normalized correlations of calcium and alkalinity revealed that surface to deep increases in calcium were 50% greater than predicted by  $\text{CaCO}_3$  flux for their data from the deep waters of the South Pacific. Alternatively, they were able to correlate calcium and carbonate alkalinity (again salinity normalized) with results much closer to the theoretical.

As pointed out by Brewer, Wong, Bacon and Spencer (1975), the "fortuitous" correlation between calcium and carbonate alkalinity of Horibe et al. (1974) was inappropriate because carbonate alkalinity is subject to changes from pressure and temperature related shifts in thermodynamic constants, as well as the dissolution of  $\text{CaCO}_3$ . Using the same data, Brewer and coworkers were able to bring the correlation of normalized calcium and alkalinity into agreement with the theoretical relationship by correcting the alkalinity values for in situ titration by acids derived from decomposing organic matter. The "potential alkalinity" lost to acids produced by the oxidation of organic matter was determined by evaluating surface to deep changes in nitrate and phosphate and added to the measured alkalinity before correlation with calcium. Therefore, rather than identifying a missing source of deep calcium, the alkalinity was shown to be lost to a previously unevaluated sink.

A similar explanation was given by Almgren, Dyrssen and Strandberg (1977) to account for the low value of the ratio of equations describing the alkalinity and calcium distribution for their data from the equatorial Pacific. The formation and decomposition of peptides and the proton shift used to balance charges in these processes were suggested to explain a value approximately 20% lower than theoretical for



the ratio of their depth and salinity dependent equations. Additionally, the data of these investigators showed a larger range in Ca/Cl (a total range of over 3%) than reported in the more recent investigations.

Dyrssen (1977) further analyzed the effect of organic matter decomposition while calculating a theoretical planktonic composition which included the  $\text{CaCO}_3$  "hard-parts". He showed that surface to deep changes in nutrients, oxygen, total  $\text{CO}_2$  and calcium yield a planktonic composition which, upon decomposition, would cause the ratio of alkalinity change to calcium change (assuming that nitrate production decreases alkalinity) to be nearly identical to that reported by Almgren et al. (1977) and within the precision of the values of Brewer et al. (1975).

The alkalinity oriented aspect of evaluating the calcium distributions was used by Chen (1978) to evaluate the decomposition of  $\text{CaCO}_3$  and organic carbon in the deep oceans following the concepts presented by Brewer et al. (1975). His work suggested that the precise alkalinity and total  $\text{CO}_2$  or nutrient data might be used to estimate changes in calcium with depth with better precision than measured calcium values were showing.

Shiller and Gieskes (1980) concluded from data collected across the Pacific Ocean along  $35^\circ\text{N}$  that while some evidence exists for the need to correct alkalinity values for in situ titration by organic matter decomposition, this effect is still poorly quantified and alkalinity "corrections" are probably of little advantage in the examination of the calcium and alkalinity distribution. Furthermore, they felt that the varied history of the waters sampled in any vertical profile is more important in explaining deviations from the theoretical  $\text{CaCO}_3$ -precipi-

tation-dissolution stoichiometry seen in other work. They suggested that boundary conditions (both "preformed" and subsequent inputs or losses) could be very difficult to evaluate.

Chen, Pytkowicz and Olson (1981) attempted to evaluate, as a first approximation, the magnitude of the lateral-mixing or "preformed" effect for waters of the deep Pacific. They used correlations of surface alkalinity and total  $\text{CO}_2$  (salinity normalized) with surface temperature to estimate "preformed" values for these properties via potential temperature (Chen and Pytkowicz, 1979). Additionally, a similar correlation was presented for calcium using the extensive data of Tsunogai et al. (1973). The results of this work showed good agreement between measured and theoretical (via the equations of Chen, 1978) increases in the calcium concentration of the deep Pacific and further suggested that as much as one-half the deep calcium increase determined in previous works was actually the result of variation in preformed quantities.

The previous work mentioned above has generally tested the various models of the calcium-alkalinity relationship without close examination of the surface and near-surface waters where most changes in calcium and alkalinity take place (Shiller and Gieskes, 1980). The work presented in the following sections of this thesis originated from an attempt to examine the calcium-alkalinity relationship and the processes which affect the calcium distribution on a finer scale in the surface and subsurface waters of the equatorial Pacific.

Prior to the analyses for calcium of samples obtained from this region, some consideration had to be given to the interference effects of other alkaline earth elements in the determination of calcium. With

a total range in Ca/Cl values generally reported to be only 1-2% of the total concentration, a technique with accuracy and precision at the 0.1% level is needed for a proper study. Complexometric titration procedures have achieved the necessary high precision, but, as described in Chapter 2, there is a great deal of uncertainty in the literature as to the magnitude of the interference of magnesium and strontium in the complexometric titration of calcium. Correction factors determined for these interferences ranging from zero to over one percent have been used and this variation, as well as the general lack of intercalibration, makes intercomparison of data sets difficult. Chapter 2 describes the technique used for analysis of the equatorial samples, the evaluation of interferences separately and together, and some values of Ca/Cl determined for IAPSO Standard Seawater. The results of this work show that no correction factor is needed for the analytical technique when applied to seawater samples, but interference effects do appear at interferant: calcium ratios higher than those found in seawater.

The results of the determination of calcium concentrations in samples from the recent transequatorial NORPAX/FGGE Shuttle are presented in Chapter 3. Evaluation of the calcium-alkalinity relationship and the overall calcium distribution in this region reveals several things. As suggested by Shiller and Gieskes (1980) "preformed" origins appear to be a very important factor in determining the shape of vertical calcium distributions. An inverse correlation was found between temperature-salinity characteristics and normalized calcium values for these samples. This work suggests that the correlation of Chen et al. (1981) for normalized calcium and surface temperature

may not be applicable in the equatorial zone, where surface waters of presently similar temperature ( $T > 22^{\circ}\text{C}$ ) yet widely varied origin come together. The surface normalized calcium distribution appears to be most consistent with the circulation features and fronts as reported for other properties in the Equatorial Pacific. This work shows the importance of physical-circulation processes in both the vertical and horizontal distribution of calcium in this complex region.

Chapter II

INTERFERENCE IN THE DETERMINATION OF CALCIUM IN SEAWATER

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## ABSTRACT

The interference of magnesium and strontium on the EGTA complexometric titration of calcium was investigated and found to be insignificant at the level of accuracy obtained in this study for the molar ratios found in seawater. Interference effects were found, however, for samples containing higher magnesium or strontium to calcium ratios. An average value of  $0.02103$  ( $SD \pm 0.00001$ ) was obtained for  $Ca:Cl^{\circ}/\text{‰}$  for nine bottles of IAPSO Standard Seawater (P79,  $19.376$   $Cl^{\circ}/\text{‰}$ ).

## INTERFERENCE IN THE DETERMINATION OF CALCIUM IN SEAWATER

As was detailed here recently (Krumgalz and Holzer, 1980), the determination of the calcium concentration of seawater is important to a variety of investigations in chemical oceanography. Studies of calcium distributions on a worldwide basis makes a convenient sea-going procedure desirable for rapid analysis of samples, ideally with precision and accuracy at the  $\pm 0.1\%$  level for good intercomparison. That this has not been available explains in part the scarcity of worldwide calcium data.

The complexometric titration, at present, best fits this need, but recent studies on complexometric determination of calcium in natural waters have differed in the end-point detection technique and the evaluation of interference by other alkaline earth elements. Studies using different end-point techniques, some of which also considered magnesium to calcium ratios in seawater, do not agree on the effect of magnesium on the titration of calcium with EGTA [ethylene glycol bis-( $\beta$  aminoethyl ether)-N-N'-tetraacetic acid]. Table 1 lists a number of these studies. The references cited report that magnesium has no effect, causes a positive interference, and, in one case, has a negative interference.

In most cases where strontium interference was evaluated, a positive interference effect was determined, but the degree of correction (on the calcium titre) varies from about  $-0.38\%$  in several studies to  $-0.77\%$  and  $-0.88\%$  in other investigations which claim all or nearly all strontium is cotitrated. With this variability in the literature, we decided to determine a correction factor for use in our visual end-

point calcium analysis. The procedure and results are presented here. We acknowledge the detailed constructive comments by F. Culkin, R. Feely, and J. P. Riley which greatly enhanced an early version of this paper.

The titration done here remains essentially unchanged from that described by Tsunogai et al. (1968a). The reagents used were prepared as described there with the exception that larger volumes of the bulk titrant were prepared and used in a continuously stirred automatic delivery system made to facilitate routine sample analysis. Air pumped into the container to replace the titrant being taken out was water saturated. Additionally, the titrant solutions were standardized against calcium carbonate of primary standard quality (JMC Puratronic, 99.9975% purity) rather than zinc, and the EGTA (Eastman Chemicals) was used without further purification. The  $\text{CaCO}_3$  used in the calcium solutions with a "seawater" matrix was Fisher Scientific Chelometric Standard (99.96% purity), whereas all other calcium solutions were made using primary standard calcium carbonate. All other chemicals used (GHA, propanol, amyl alcohol,  $\text{NaCl}$ ,  $\text{MgSO}_4$ , and  $\text{SrCl}_2$ ) were Fisher Scientific reagent grade chemicals.

Twenty-five milliliters of a titrant strong enough to complex about 98% of the dissolved calcium were added to samples of 25 ml (30 ml in the lower "salinity" determinations and 22 ml in the higher "salinity" determinations). GHA-propanol reagent (4 ml) and the borate buffer (4 ml) were added to this solution. This was stirred rapidly for about three minutes and the amyl alcohol (5 ml) added. The solution was then stirred vigorously and dilute EGTA titrated under fluorescent lighting via a micrometer piston-buret (Gilmont, 2.5 ml



capacity) until a faint pink color remained. At this point the titration became a series of small additions with vigorous stirring followed by periods in which the immiscible layers separated and the organic layer was checked for remaining red color. This process was continued until all the red color was gone. Reagent blanks were done with each batch of samples using 50 ml of distilled-deionized water in place of sample and initial titrant. The blank volume was subtracted from the dilute titrant volume in the calculation of calcium concentration. Reagent blanks were typically less than 1  $\mu\text{M}$ .

The results of this study are summarized in Tables 2, 3, and 4. Table 2 shows the actual and measured concentrations for solutions of varied calcium content and "salinity". Table 3 shows the amount of calcium measured in solutions containing calcium and each individual alkaline earth in various ratios. Table 4 shows the amount of calcium measured in solutions of the high "salinity" matrix and of the individual salts. The solutions of the high purity  $\text{CaCO}_3$  were accurate to about  $\pm 4 \mu\text{M}$  and those of "salinity" matrix are probably accurate to  $\pm 6 \mu\text{M}$ . The corrected values for calcium have had the appropriate amount of calcium subtracted as indicated in Table 4 (which indicates calcium impurities consistent with those listed for the reagents used). The determined calcium concentration listed in the tables is the average of two trials which typically differed by 2 or 3  $\mu\text{M}$  at most unless otherwise indicated. This is similar to the precision ( $1 \sigma$ ) shown in the data of Tsunogai et al. (1968a).

It is apparent in the data of Table 2 that the presence of normal concentrations of sodium, magnesium and strontium have no net effect on this determination of calcium above the approximate level of accu-

racy of about 0.1%. Thus, for our titration of calcium no correction factor seems necessary. It is important to point out that a sufficient amount of titrant needs to be added to complex at least 98% of dissolved calcium before the buffer is added. This apparently reduces the loss of calcium due to coprecipitation with  $Mg(OH)_2$ .

Although our result differs from the findings of Culkin and Cox (1966) and of Tsunogai et al. (1968a), it does not disprove the possible cancellation of positive and negative corrections as indicated in the data of Tsunogai et al. (1968a). The data of Table 3 indicate that there is no effect above 0.1%. At higher molar ratios of magnesium or strontium the interference effects begin to appear. As reported by Tsunogai et al. (1968a) the interference of magnesium appears to be negative and as stated there (for strontium) is related to the extraction into the organic layer of the calcium-GHA complex. A positive interference was determined for strontium at twice the seawater molar ratios. Therefore the interferences of the individual alkaline earth elements on the calcium titration determined here are consistent in direction, though clearly not in magnitude, with those reported by Tsunogai et al. (1968a). Additionally, the presence of sodium (chloride) in the solutions seems to diminish these interference effects in both cases. It is not clear why this should be and we have no obvious explanation at present for the reduced interference effect when sodium is present. It does suggest the advantage of either standardizing the titrant against a seawater matrix calcium standard or having some matrix available in evaluating individual interference effects on a procedure to be used for seawater samples.

Other types of interference (e.g. with the indicator, Goldstein

and Stark-Mayer 1958; Goldstein 1959) are not apparent in the data and examination of the titrant-cation stability constants is of limited use. The magnitude of the stability constants ( $10^{11}$ ,  $10^{8.5}$ ,  $10^{5.2}$  for Ca, Sr, and Mg: Schwarzenbach and Flaschka 1969) suggests the possible interference of strontium even at its approximate 1% molar ratio to calcium in seawater. A more appropriate evaluation of "conditional" constants (Schwarzenbach and Flaschka 1969) or at least a first approximation of these constants (calculated considering only the effect of the other two cations on each individual at the concentrations found in 35‰ salinity seawater) yields values of  $10^{6.5}$ ,  $10^{-0.5}$ , and  $10^{-3.8}$  for Ca, Sr, and Mg. This would seem to indicate sufficient separation for titration, although the reduction in the calcium-titrant stability constant results in reduced titration accuracy (Schwarzenbach and Flaschka 1969)<sup>1</sup>. This is a simple evaluation of the system though, and doesn't consider all the conditions of the titration (e.g. magnesium precipitation, alcohol extraction). The empirical approach, as taken here and by others, would seem most useful at present.

In determining the calcium concentration in seawater samples, IAPSO Standard Seawater has been used as a running standard for inter-comparison purposes. For example, P79 (19.376‰ Cl) was used as the standard over a period of seven months. The calcium concentration determined for this seawater was  $10,408 \pm 3$  (2  $\sigma$ )  $\mu\text{M}$  (9 determinations), which was equivalent to  $10,167 \mu\text{mol kg}^{-1}$  or  $0.02103 \text{ g kg}^{-1}$ : ‰ Cl. Table 5 shows values reported for Standard Seawater. The values

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1. A more detailed discussion of the "conditional" constants and the resulting theoretical titration curves is presented in Appendix 1.

reported for this work are generally lower, without negative correction, than those reported elsewhere. It should be noted, however, that the varied origin of different batches may contribute to offsets in addition to analytical errors.

Until more intercomparison work is done on identical samples, as suggested by Culkin and Cox (1966), little can be said to explain the variation in data. This study, however, indicates that the procedure of Tsunogai et al. (1968a) basically meets the analytical requirements mentioned.

Table 1. Recent reported studies on the determination of calcium using EGTA titration.

Reference	Method	Conclusion
Schmid and Reilley 1957	Hg-electrode	No Mg interference at seawater ratios
Ringbom et al. 1958	Zn-Zincon	Positive Mg interference from Mg:Ca $\sim$ 1.5 and higher
Sadek et al. 1959	Zn-Zincon	No Mg interference at seawater ratios
Wanninen 1961	Theoretical, Zn-Zincon	Titration error if Mg > Ca
Date and Toei 1963	Various chemical visual indicators	No Mg interference at seawater ratios when end-points sharp
Culkin and Cox 1966	Zn-Zincon	Mg interference of +0.729% on Ca titre; Sr interference of +0.388% on Ca titre
Tsunogai et al. 1968a	GHA	Mg interference of -0.23% on Ca titre; Sr interference of +0.77% on Ca titre
Schwarzenbach and Flaschka 1969	Stability constants "conditional constants"	Sr interference; Increased titration error at seawater ratios -- dependent upon end-point sensitivity
Horibe et al. 1974	Cal-Red	Sr interference of +0.37% on Ca titre
Jagner 1974	Computer simulated curves of Zn-Zincon	Mg interference at seawater ratios
Lebel and Poisson 1976	Amalgamated-Ag electrode	No Mg interference; Sr interference of $\sim$ +0.9% on Ca titre
Krumgalz and Holzer 1980	Ca-ion selectrode	No Mg interference
Kanamori and Ikegami 1980	Ca-ion selectrode	No Mg interference; No Sr interference

Table 2. Study of net interference on calcium determination in artificial seawater. The major groupings of calcium concentration approximate that found at 30 ‰, 35 ‰, and 40 ‰ salinity.

cCa <sup>*</sup>	cNa:cCa <sup>†</sup>	cMg:cCa <sup>†</sup>	10 <sup>3</sup> cSr:cCa <sup>†</sup>	cCa <sup>*</sup> measured	cCa <sup>†</sup> corrected	Δ <sup>§</sup>
8,845	0	0	0	8,841	8,841	-0.05%
8,841	45.6	0	0	8,838	8,834	-0.08%
8,841	45.6	5.2	8.8	8,838	8,833	-0.09%
8,943	0	0	0	8,946	8,946	0.03%
8,935	45.1	0	0	8,934	8,930	-0.06%
8,935	45.1	5.1	8.7	8,934	8,929	-0.07%
10,321	0	0	0	10,322	10,322	0.01%
10,305	45.6	0	0	10,314	10,310	0.05%
10,305	45.6	5.2	8.8	10,316	10,311	0.06%
10,423	0	0	0	10,419	10,419	-0.04%
10,415	45.1	0	0	10,426	10,422	0.07%
10,415	45.1	5.1	8.7	10,426	10,421	0.06%
11,782	0	0	0	11,785	11,785	0.03%
11,782	45.6	0	0	11,786	11,782	0.00%
11,782	45.6	5.2	8.8	11,784	11,775	-0.06%
11,902	0	0	0	11,906	11,906	0.03%
11,902	45.1	0	0	11,910	11,906	0.03%
11,902	45.1	5.1	8.7	11,906	11,897	-0.04%

<sup>\*</sup> Calcium concentrations reported in μM, actual concentration based on in vacuo mass.

<sup>†</sup> All ratios are molar: ratios approximate those of seawater.

<sup>‡</sup> Correction by subtraction of appropriate blank solution calcium concentration, 4 μM from solutions containing sodium, 5 from the lower two "salinity" matrices and 9 from the high "salinity" matrix.

<sup>§</sup> Δ = 100 (corrected - actual)/actual.

Table 3. Study of separate alkaline earth elements interference.

Solution composition ( $\mu\text{M}$ )	cCa measured	cCa corrected	$\Delta^*$
10,399 Ca	10,402	10,402	+0.03%
10,399 Ca, 54,000 Mg	10,396 ( $\pm 5$ ) <sup>†</sup>	10,395	-0.04%
10,399 Ca, 54,000 Mg, 470,000 Na	10,401	10,396	-0.03%
10,399 Ca, 108,000 Mg	10,340 ( $\pm 10$ ) <sup>‡</sup>	10,338	-0.59%
10,399 Ca, 108,000 Mg, 470,000 Na	10,396	10,390	-0.09%
10,399 Ca, 216,000 Mg	10,180 ( $\pm 20$ ) <sup>§</sup>	10,176	-2.10%
10,399 Ca, 216,000 Mg, 470,000 Na	10,300 ( $\pm 10$ )	10,292	-1.00%
10,399 Ca	10,402	10,402	+0.03%
10,399 Ca, 91 Sr	10,405	10,404	+0.05%
10,399 Ca, 91 Sr, 470,000 Na	10,400	10,395	-0.04%
10,399 Ca, 182 Sr	10,430 ( $\pm 10$ ) <sup>  </sup>	10,429	+0.28%
10,399 Ca, 182 Sr, 470,000 Na	10,417	10,411	+0.12%

\*  $\Delta = 100 (\text{corrected} - \text{actual}) / \text{actual}$ .

<sup>†</sup> End-point color change different -- less sharp.

<sup>‡</sup> End-point much less sharp -- organic layer clear, bulk solution orange-pink.

<sup>§</sup> End-point much less sharp -- nearly no color extracted into organic layer after bulk titrant addition.

<sup>||</sup> End-point color change slightly different -- greenish.

Table 4. Study of calcium impurities in reagents  
used to prepare salt matrix.

Solution composition ( $\mu\text{M}$ ) <sup>*</sup>	cCa measured ( $\mu\text{M}$ )
Na 403,000, Mg 46,000, Sr 78	6
Na 470,000, Mg 53,000, Sr 91	4
Na 537,000, Mg 60,800, Sr 104	9
Sr 91	$\leq 1$
Mg 53,000	1
Na 470,000	4

\*The three mixed salt solutions approximate 30 ‰, 35 ‰, and 40 ‰ salinity.



Table 5. Ca:Cl values determined for Standard Seawater using EGTA titrations.

g kg <sup>-1</sup> ; ‰ Cl	Batch	Correction	Reference
0.02122	P33	negative Mg, Sr	Culkin and Cox 1966
0.02127	unspecified	implicit in titre standardization	Jagner 1974
0.02109	P61	unspecified	Shiller and Gieskes 1980
0.02130	P73	none	Krumgalz and Holzer 1980
0.02122	unspecified	none	Kamamori and Ikegami 1980
0.02114	P78	none	this work
0.02103	P79	none	this work
0.02106	P86	none	this work

CHAPTER III

THE DISTRIBUTION OF CALCIUM IN THE EQUATORIAL PACIFIC OCEAN

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## ABSTRACT

Calcium concentrations were measured in seawater samples of the upper 1000 m obtained from two legs of the recent Hawaii-Tahiti Shuttle Experiment (Legs 3 and 13). Values of normalized calcium (to 35‰ salinity) ranged from 9,967 to 10,354  $\mu\text{mol kg}^{-1}$  (0.02063 to 0.02142 gm Ca  $\text{kg}^{-1}$ : ‰ Cl) with the low values consistently correlating with warm surface waters of high salinity. The higher normalized calcium values were associated with waters from higher latitudes, which were evident in these transects either as upwelled intermediate water or as water circulated around the central gyres. Comparison of  $\theta$ -salinity,  $\theta$ -calcium (normalized) and  $\theta$ -alkalinity (normalized) diagrams suggests that water history or "preformed" values are more important factors in the vertical distribution of calcium than local vertical production and dissolution of  $\text{CaCO}_3$  for near surface waters of this region. Circulation features (e.g. equatorial currents and upwelling of intermediate waters) are evident in cross-sectional comparisons of normalized calcium values on the transect along 158°W. This probably reflects the varied "preformed" values of waters that come together in the equatorial region.

## INTRODUCTION

In the last twenty years a number of investigators have attempted to evaluate (in some respect) the spatial and/or temporal distribution of calcium and the ratio Ca/Cl in the world's oceans. The temporal variability of Ca/Cl is not yet well defined (BILLINGS, BRICKER, MACKENZIE and BROOKS, 1969; ATWOOD, FROELICH and KINARD, 1973) whereas studies on the vertical distribution have consistently shown a significant increase in calcium (on a constant salinity basis) in deep waters. This essentially confirms the early findings of DITTMAR (1884) who was also among the first to compare this increase with similar changes in alkalinity, thus supporting the concept of surface  $\text{CaCO}_3$  precipitation and subsequent dissolution at depth.

Numerous recent investigations of calcium's spatial distribution have been undertaken using new complexometric titration techniques and ion specific chelators (e.g. EGTA for calcium). Nearly all recent works show the increase in normalized calcium with depth (CULKIN and COX, 1966; RILEY and TONGUDAI, 1967; TSUNOGAI, NISHIMURA and NAKAYA, 1968b; SAGI, 1969; TSUNOGAI, YAMAZAKI and NISHIMURA, 1971; TSUNOGAI, YAMAHATA, KUDO and SAITO, 1973; HORIBE, ENDO and TSUBOTA, 1974; ALMGREN, DYRSSEN and STRANDBERG, 1977; SHILLER and GIESKES, 1980), and many show considerable variation in the surface values of Ca/Cl (TSUNOGAI *et al.*, 1986b; SAGI, 1969; TSUNOGAI *et al.*, 1971; ALMGREN *et al.*, 1977; SHILLER and GIESKES, 1980). Some discussion has been made on the use of Ca/Cl as a water mass tracer (TSUNOGAI *et al.*, 1968b) and the relation between calcium and nutrients in surface waters (TSUNOGAI *et al.*, 1971), but much of the work has been directed towards correla-

ting the calcium increases at depth with similar increases in alkalinity.

Improved precision in calcium analyses has shown that the simple  $\text{CaCO}_3$  precipitation-dissolution concept can not be successfully modeled by calcium and alkalinity data alone (TSUNOGAI *et al.*, 1973; HORIBE *et al.*, 1974; ALMGREN *et al.*, 1977). Several investigators have shown that the apparent excess of calcium in deep waters may result from decreases in alkalinity brought about by the oxidation of organic matter (BREWER, WONG, BACON and SPENCER, 1975; ALMGREN *et al.*, 1977) and have been able to better correlate calcium increases with those of "corrected" alkalinity. SHILLER and GIESKES (1980), however, have recently observed that the lateral-mixing nature of the ocean may play a more important role in the vertical calcium and alkalinity distribution because of variation in "preformed" or boundary conditions and water history, conclusions similar to those of others who have recently investigated the distribution of some chemical "tracer" (KEELING and BOLIN, 1968; EDMOND, JACOBS, GORDON, MANTYLA and WEISS, 1979; FINE, REID and OSTLUND, 1981).

CHEN, PYTKOWICZ and OLSON (1981), in an attempt to make a first approximation of the magnitude of these lateral or "preformed" effects, used correlations of surface temperature with alkalinity, total  $\text{CO}_2$ , and calcium (all salinity normalized) (using the equations of CHEN and PYTKOWICZ, 1979 and the data of TSUNOGAI *et al.*, 1973) to calculate the surface origin value for each of these parameters via potential temperature. The results showed good agreement between measured and theoretical (via "corrected" alkalinity) increases in the calcium concentration in the deep water of the Pacific. Additionally, this work

suggested that, perhaps as much as half the increase seen in deep water values of calcium in prior work may actually result from greater "preformed" values, instead of from local  $\text{CaCO}_3$  dissolution. Unfortunately, although the calcium concentration was found to correlate with alkalinity to within the combined precision of the data on a large scale, finer scale detailed comparison was not possible due to the large vertical spacing of samples and the large uncertainty of the data. Furthermore, though the empirical preformed calcium- $\theta$  equation given by CHEN *et al.* is the best available, it is not clear whether the equations adequately represent the calcium data above  $20^\circ\text{C}$ .

The recent NORPAX/FGGE transequatorial shuttle program provided us with an opportunity to study the calcium and alkalinity relationship and the processes which affect it on a finer scale in the upper 1000 m in a region where waters from a variety of surface origins come together. The input of waters from higher latitudes and the influence of the equatorial current system provide a unique area for study of the calcium distribution and the results of our measurements on samples from two legs are presented here.

## EXPERIMENTAL

Samples were collected for us on legs 3 (April, 1979) and 13 (March-April, 1980) of the Hawaii-Tahiti Shuttle experiment. The samples from leg 3 were collected from casts made along 158°W on a transect from 4°S to 16°N by 2° and 4° intervals and include depths from 2 to about 1000 meters. These samples were stored in polyethylene bottles protected from light and were analyzed over the next two years. The samples from leg 13 were collected from the two southernmost stations (17°, 16°S), the two northernmost (21°, 20°N), and two intermediate stations (4°S, 4°N) and samples again ranged from 2 to 1000 meters. These were stored in opaque polyethylene bottles and analyses were completed within four months of collection of the oldest sample. All hydrographic and nutrient data, and some alkalinity data for leg 3 (for comparison) were obtained from the HAWAII-TAHITI SHUTTLE EXPERIMENT HYDROGRAPHIC DATA REPORTS volumes I and IV (1981).

Calcium Analysis

The calcium content of the seawater samples was measured using the technique of TSUNOGAI, NISHIMURA and NAKAYA (1968a) with minor modifications and without correction for the presence of magnesium and/or strontium. The procedure, standardization, evaluation of correction factor, and values of Ca/Cl determined for IAPSO Standard Seawater which was used as a running standard are described in Chapter 2. Values measured for calcium are the average of two titrations which rarely differed by more than 5  $\mu\text{M}$  (in which case a third titration was often done if there was enough sample left).

Salinities were determined at the time of analysis using an Auto-

sal inductive salinometer in most cases and high precision density measurements for the others. These salinities were used to determine densities of the samples and to correct measured values back to original salinity after storage. The analytical precision for routine replicate sample analyses is estimated to be  $\pm 10 \mu\text{mol kg}^{-1}$  ( $2\sigma$ ), but the overall precision after correction for evaporation during storage may be better estimated as  $\pm 15 \mu\text{mol kg}^{-1}$  ( $2\sigma$ ).

Evaporation of leg 3 samples proved to be a problem particularly among the last to be analyzed. A large percentage of those samples with about 0.25‰ or more evaporative change in salinity exhibited anomalously low Ca/Cl and nearly always a coincident low specific alkalinity, presumably due to the precipitation of  $\text{CaCO}_3$ . It is not known whether this occurred as inorganic precipitation or was biologically mediated. No attempt was made to correct for this and the concentrations measured for these samples are not included in the data used here. The leg 13 sample containers did not allow much evaporation ( $<0.05\%$  salinity at analysis time) and only three samples are suspect (discussed later). Approximately one year later, several leg 13 samples (total evaporation  $<0.10\%$  salinity at analysis time) were reanalyzed and gave essentially identical results.

#### Alkalinity Analysis

Alkalinities were determined using a slight modification of the single acid addition technique described by CULBERSON, PYTKOWICZ and HAWLEY (1970). Smaller volumes of sample and acid were used and a value of 0.71 was used for  $f_H$  in calculating the result (CULBERSON and PYTKOWICZ, 1973; JOHNSON, VOLL, CURTIS and PYTKOWICZ, 1977). Both analytical and overall precision are estimated to be  $\pm 8 \mu\text{eq kg}^{-1}$  ( $2\sigma$ ).



The alkalinities determined for the leg 13 samples are approximately  $25 \mu\text{eq kg}^{-1}$  lower than nearby GEOSECS stations (TAKAHASHI, BROECKER, BAINBRIDGE and WEISS, 1980). The measured alkalinities of leg 3 samples seem to be subject to varying systematic (station by station) disagreement with those reported in the Hydrographic Report-I. While our alkalinity data is precise enough for vertical comparison with the calcium data on a station to station basis, the data of the Hydrographic Report (with some adjustment) is better for a cross section comparison.

## RESULTS AND DISCUSSION

Several comments on the data sets should be made prior to discussion of the distribution of calcium and of processes affecting it. The range of normalized calcium values found is from 9,967 to 10,354  $\mu\text{mol kg}^{-1}$  (0.02062 to 0.02142  $\text{gm kg}^{-1}$  Ca per ‰Cl), a range of about 3.8%. However, only two values below 10,000  $\mu\text{mol kg}^{-1}$  were found, and while these samples did not exhibit the other characteristics previously discussed concerning carbonate precipitation during storage, they alone are well below the next lowest value of 10,045  $\mu\text{mol kg}^{-1}$  (0.02078) and are suspect. It should be pointed out that a range in normalized calcium values of 3% results in relative deviations in salinity and sigma- $\theta$  of 0.1% (calculated as the result of  $\text{CaCO}_3$  dissolution as shown by BREWER and BRADSHAW, 1975). These deviations would affect the calcium data presented by an amount less than the probable precision and will not be considered here.

The range found here is over twice as large as that reported by CULKIN and COX (1966) for samples from all oceans and that of TSUNOGAI *et al.* (1973) for their sampling in the Pacific Ocean. However, our range of values is in good agreement with that reported by SAGI (1969) and, after systematic adjustment of data sets, with that of ALMGREN *et al.* (1977), both of which were studies of the equatorial Pacific Ocean. At present, it is unclear why such differences exist in the overall range reported by analysts using techniques both similar to (SAGI; TSUNOGAI *et al.*) and different from (CULKIN and COX; ALMGREN *et al.*) this work. As mentioned in Chapter 2, some intercalibration effort seems necessary to ascertain the relative magnitudes of the

natural and analytical contributions to this uncertainty. Despite these variations, the data used in this work appear to present a consistent overall picture.

#### The vertical distribution of calcium and the calcium-alkalinity relationship

The vertical distribution of calcium (or salinity normalized calcium) has been associated with the alkalinity distribution via the calcium carbonate precipitation-dissolution model. Work on this problem has largely centered upon the agreement or disagreement between calcium and alkalinity changes (from a reference of choice) in deep water and has rarely closely examined the relationship between the two quantities in the surface and near surface waters. However SHILLER and GIESKES (1980) pointed out that major changes in calcium and alkalinity take place above 1500 m, a region where lateral effects may overshadow simple vertical processes. Surface and subsurface waters (to 1000 m depth) are the subject of study here.

The vertical profiles of calcium concentration reflect mainly only the variation of salinity with depth, as would be expected for an element which is nearly conservative. Figure 1 is the cross section for salinity from 4°S to 21°N along 158°W from leg 3 and clearly demonstrates the complexity (seen as salinity extrema in vertical profiles) of this region. More interesting is the distribution of normalized (to 35‰ salinity) calcium (NCa) with depth or, as is shown in Fig. 2, a comparison of  $\theta$ -salinity with  $\theta$ -Nca diagrams. These comparisons, with the exceptions of those stations where too few values of NCa are available, generally show a mirroring of salinity and NCa.

That is, in the salinity maxima the NCa values generally become minima and vice versa. This is evident in the well defined profiles for leg 3 stations (especially 3-82 and 3-86 where several extrema resulting from the influence of the water from higher latitudes are reflected).

Comparison of  $\theta$ -S plots from the hydrographic data with the continuous CTD profiles reveals that there is a fine structure unresolved in the bottle salinity data that may better correlate with the few NCa values which appear anomalous. The correlation is also quite clear in the leg 13 profiles with the obvious exception of station 13-61 at 4°S. The deepest three samples at this station all appear to be offset to lesser values of NCa without showing any increase in salinity. Reanalysis of the entire profile gave identical results. This feature also seems to appear to a much smaller extent in the profiles of 3-64 (4°S) and 3-66 (2°30'S). The hydrographic data show very slight minima in oxygen and maxima in nutrients at the depth of the offset. However, this would seem to be too severe an offset to exist in a region of smooth salinity change and may be the result of CaCO<sub>3</sub> precipitation after sampling although we can not be sure because the alkalinity measured (as will be shown) only shows a slight offset.

The correlation between warm, high salinity surface waters and low specific calcium has been noted previously (TSUNOGAI *et al.*, 1968b; SAGI, 1969; TSUNOGAI *et al.*, 1971; TSUNOGAI *et al.*, 1973) and has generally been attributed to biological depletion in warm tropic and subtropic waters. While biological variability is certainly at least partly responsible for differences in "preformed" NCa values, these comparisons indicate that the "preformed" quantities, regardless of the processes that regulate them in the surface waters, are more important

than local production and dissolution of calcium in determining the vertical distribution of calcium in the upper 1000 m of the equatorial Pacific Ocean. The variability of biological activity is more directly evident in side-by-side or cross-sectional comparisons as will be shown later.

These results are consistent with the suggestions of SHILLER and GIESKES (1980) concerning the near surface vertical distribution of calcium and the recent comments of others on the importance of lateral influence in vertical profiles (EDMOND *et al.*, 1979; FINE *et al.*, 1981). The relationship between normalized calcium and water origin (as indicated by salinity and temperature) suggests that a simple correlation between calcium and alkalinity or "corrected" alkalinity (BREWER *et al.*, 1975; CHEN, 1978) is unlikely unless, of course, the alkalinity shows similar "preformed" variability in vertical profiles. Figure 3 shows the normalized (to 35‰ salinity) titration alkalinity (NTA) plotted with potential temperature for each of the six leg 13 stations (note again the offset for the deep samples of 13-61) and these diagrams do not, at first glance, suggest such a clear dependence on water origin. Thus, simple correlations of normalized calcium and normalized and/or corrected alkalinity may not be applicable in this complicated oceanic region.

Though accurate evaluation of the "preformed" correction needed in calcium-alkalinity comparisons may be difficult (SHILLER and GIESKES, 1980), more information might be obtained by using the first approximations of CHEN *et al.* (1981). The dashed lined in the leg 13 profiles of NTA (Fig. 3) represent the "preformed" alkalinity-potential temperature correlations given by CHEN and PYTKOWICZ (1979) and used by CHEN

*et al.* In general these figures indicate (if the preformed lines are reasonably accurate) that alkalinity has been consumed in waters at or slightly below their "surface origin". It is worth noting that this "preformed" alkalinity line is constructed from preliminary GEOSECS data and the recent carbonate chemistry report of TAKAHASHI *et al.* (1980) gives alkalinity data that is systematicall higher. Whether or not the alkalinity data used here is then also systematically increased to agree with the higher GEOSECS values will not affect the relative (within the vertical profile) differences between measured and preformed values. The consumption seems entirely reasonable, via carbonate precipitation, without implying that it is a strictly local-vertical process. However, the profiles show increasing loss of alkalinity with depth to the point where the influence of intermediate water begins (at about 6 or 7°C in the south and about 10°C elsewhere), whereas the calcium profiles (Fig. 2) appear to indicate the heaviest calcium consumption nearer to the surface waters. This could perhaps result from the effect of organic matter production-decomposition on alkalinity (BREWER *et al.*, 1975; BREWER and GOLDMAN, 1976), offsetting some of the loss of alkalinity to carbonate production in the near surface by nitrate uptake and contributing to alkalinity loss in the subsurface water via decomposition of organic matter. At about 8°C (coinciding with the fresher intermediate waters) the normalized alkalinity begins to increase sharply while potential temperature decreases. This trend continues well into the deep water at nearby GEOSECS stations (235,237) and may represent several factors, such as the decreased production of  $\text{CaCO}_3$  in surface waters colder than 10°C where siliceous organisms begin to dominate (BE, 1960; McINTYRE, BE and ROCHE, 1970; LISITIZIN, 1972) or, possibly, the increase associated

with mixing in deeper, higher alkalinity waters (although NCa values show a decrease below the intermediate water which will be discussed later).

Using the normalized calcium-potential temperature correlation of CHEN *et al.* (1981) on these NCa- $\theta$  plots (Fig. 2) is more difficult because all surface waters in this study are well above 20°C, the temperature above which CHEN *et al.* assign a single normalized calcium value. These data show that the equatorial surface waters of varied origins, but presently similar temperatures, can not be successfully modeled by this correlation. Additionally, the range of this data set is larger than that of TSUNOGAI *et al.* (1973) whose data were used to make the correlation and it seems unlikely that the slope in surface temperature-NCa correlation produced in that work would be accurate for these data. Consequently, it may be more appropriate to make qualitative observations and comparisons with the alkalinity profiles.

Despite the lack of a "preformed" line on the NCa- $\theta$  plots, it appears that calcium has been consumed in warmer, higher salinity waters that are now at, or slightly below, the surface. The other extremes in the NCa profiles always occur coincident with waters lower in salinity and temperature, presumably from higher latitudes, whether upwelled or part of the general circulation (REID, 1965; 1973). The increased NCa values in this water may represent both higher "preformed" values and/or the local mixing influence of deeper (higher specific calcium) waters. However, as these waters rarely penetrate deeper than 1000 m (REID, 1965) they may not be subject to much local input of dissolved-carbonate calcium. Saturation state calculations, using the NCa data, the CO<sub>3</sub> data (normalized) of the Hydrographic

Report (HAWAII-TAHITI SHUTTLE EXPERIMENT, I, 1981) and the calcite solubility expressions of INGLE (1973), indicate that all samples (assuming the leg 13 carbonate data to be approximately equal to the leg 3 data) are supersaturated or within 10% of saturation with respect to calcite (however, aragonite saturation states are as low as approximately 50% in some of the deeper samples and this may be of some importance since pteropods have been found in the Pacific Equatorial region; P. BETZER, personal communication, 1981). TSUNOGAI *et al.* (1973) show in their Ca/Cl cross section of the Pacific Ocean that the intermediate waters tend to maintain constant Ca/Cl as they proceed toward the central Pacific, therefore it would appear that this maximum in normalized calcium reflects increased "preformed" values alone. Consistent with this is the decrease in NCa seen just below the intermediate water and corresponding to a slight salinity increase. This feature does not appear in the NTA- $\theta$  figure and at first glance it suggests that the surface correlation of normalized calcium and temperature should show decreased NCa values at temperatures colder than those of the intermediate waters (rather than the increased NCa values predicted by the correlation of CHEN *et al.*) while the alkalinity correlation should not. This decrease in NCa or Ca/Cl below intermediate waters is also evident in the data of TSUNOGAI *et al.* (1973) in much of the Pacific. Examples are seen in their figures 2 and 3 at about 1 km (the upper 1500 m of which are redrawn against potential temperature here in Fig. 4). We can only speculate that this water has "origins" other than the surface of the Pacific Ocean and that these origins contain significantly lower normalized calcium while differing much less in alkalinity than the water which currently lies above it.



This is consistent with the speculations of TSUNOGAI *et al.* (1971, 1973) that the Ca/Cl value is less in the Atlantic Deep Water and Antarctic Circumpolar Water than the mean value for the Pacific Ocean water, but this implies that this water hasn't mixed to any great extent with deep Pacific (high calcium) water. Such a difference may not be as great in alkalinity or, alternatively, it may be more difficult to detect in alkalinity data due to the lesser relative precision and possible organic matter effects.

The conclusions drawn from these vertical profiles, then, suggest that for waters of the upper 1000 m in the equatorial Pacific, the "preformed" values or surface origin calcium concentration is the most important factor determining relative extrema in vertical calcium profiles and that the single surface temperature-normalized calcium value used by CHEN *et al.* (1981) does not adequately describe the variation in surface waters near the equator. The point must be stressed, however, that this data set and these conclusions apply only to the surface equatorial region which is an area of considerable variability in surface water history. The "preformed" correlation of CHEN *et al.* may adequately model the changes from high salinity gyre to the regions of intermediate water formation and beyond. These results do not affect any of the previous correlations of calcium and alkalinity in the relatively uniform deep waters. The key to that work is, of course, the accuracy of the reference values chosen.

#### The horizontal-transequatorial distribution of calcium

Figure 5 shows the cross-sectional distribution of normalized calcium along 158°W from 4°S to 16°N for leg 3. This figure demonstrates

the influence of circulation processes on the calcium distribution in this region. The dashed contour lines connecting the 20° and 21°N stations of leg 13 indicate the uncertainty in continuity between data of different years. It should be pointed out that the contour lines drawn (especially the dashed lines) are subject to interpretation considering both the analytical uncertainty and the sparsity of samples, particularly in the north portion of the transect and at depths below 500 m.

The lowest values of normalized calcium in the cross section are associated with the high salinity water of the subtropic gyres (Fig. 1), a feature seen previously in the mid latitudes of the Pacific (SAGI, 1969; TSUNOGAI *et al.*, 1973) as well as in the Indian Ocean (TSUNOGAI *et al.*, 1971). As suggested in these previous reports, the low calcium concentrations, like the low nutrient concentrations, may result from biological utilization in waters that are relatively unmixed. The longer residence time of water within the southern gyre (MONTGOMERY, 1959) may explain why both lower Nca values and higher salinities are found in the south. At the southern end of the transect the low normalized calcium values extend (allowing for sample spread) to the region of the Equatorial Undercurrent (EUC) which is generally thought to contain a large component of southern waters of higher salinity (TSUCHIYA, 1968; REID, 1973).

The remaining features in the surface layer distribution of Nca appear to correlate best with the circulation features as seen in cross sections of measured currents (WYRTKI, FIRING, HALPERN, KNOX, McNALLY, PATZERT, STROUP, TAFT and WILLIAMS, 1981) and geostrophic zonal velocities (TAFT and KOVOLA, 1979). Strict comparison with velocity cross

sections from other years and/or months of the year may not correlate exactly as these equatorial circulation features change strength and shift location somewhat on the time scale of months (TAFT and KOVALA, 1979; WYRTKI *et al.*, 1981). Nevertheless, general comparison of the normalized calcium contours with the boundaries between the equatorial currents shows good agreement. From about 4°N to 9°N in the upper 200-300 m there is a relative low in normalized calcium. This feature appears to coincide with the North Equatorial Countercurrent (NECC). As in the case of the EUC, the NECC may have some component of southern origin water (TSUCHIYA, 1968), which may explain in part why the NCa values are relatively low here. Increased biological utilization may also be a factor as nutrient data show upwelling centered about 8°N.

The relative high NCa values centered at about 2°N lies in what would probably be considered the northernmost edge of the South Equatorial Current (SEC). The cause for this relative high is uncertain, but we can speculate on the origin of this water. This water may be part of the surface circulation from the southern ocean which is relatively unaffected by calcium consumption (or perhaps has a very small component of water from the gyre). Alternatively this water may be largely from the Eastern Tropical Pacific, a region of low oxygen (TSUCHIYA, 1968) and low tritium (FINE *et al.*, 1981), indicating possible recent upwelling and therefore probably having higher normalized calcium values.

Similar speculations may be made for the surface waters between about 10° and 16°N, in what is considered the North Equatorial Current (NEC). At its southern limit there is a reasonably sharp front

(though the data are very sparse in this region) between the NECC and the NEC. This is consistent with the tritium front shown by FINE *et al.* (1981) and the tritium-based model of exchange between these currents, which showed very little flux across the boundary (FINE and OSTLUND, 1981). Here, however, the higher tritium values in the NEC tend to suggest that transport from the north is a more important influence than that of the Eastern Tropical Pacific. SHILLER and GIESKES (1980) also show increased NCa values in the California Current, which turns west into the NEC.

In effect, this northern front continues at depth, with the influence of water from higher latitudes quite obvious down to at least 500 m. The sigma-theta values for the samples at 16°N suggest that this water (and the higher NCa values found here) may be the result of anticyclonic circulation, as shown for tritium (FINE *et al.*, 1981), rather than upwelling. Below this too few data points are available to make much comment but the overall picture appears consistent, in terms of this front or boundary between equatorial subsurface waters and those from further north, with the conclusions of others for the Pacific Ocean (SVERDRUP, JOHNSON and FLEMING, 1942; TSUCHIYA, 1968; FINE *et al.*, 1981) and also recently discussed for the Atlantic (BROECKER and OSTLUND, 1979).

The remaining major feature is the increased NCa values seen in the southern portion of the transect below 300 m. This may represent the northernmost remnant of the Antarctic Intermediate Water and the higher "preformed" values found there as discussed earlier. Further evidence for this is a distribution of maximum "NO" values (BROECKER, 1974) similar to the southern high in normalized calcium. The "NO"

values in this region where NCa is greater than  $10.30 \text{ mmol kg}^{-1}$  are between 425 and  $450 \text{ } \mu\text{mol kg}^{-1}$ . A plot of "NO" versus salinity (as in BROECKER, 1974, figure 8) for Pacific GEOSECS data shows that the Pacific Ocean AAIW should have "NO" values between 430 and  $450 \text{ } \mu\text{mol kg}^{-1}$  by the time it has achieved salinities between 34.5‰ and 34.6 ‰ in the equatorial region.

The normalized calcium distribution then, seems to follow a pattern in the equatorial Pacific surface waters that is consistent with, and to a large extent dependent upon, circulation features. It would appear that longer residence times in southern high salinity waters and the subsequent distribution of those waters results in the surface calcium distribution observed south of the NEC. As seen by others (SVERDRUP *et al.*, 1942; TSUCHIYA, 1968; REID, 1973; FINE *et al.*, 1981) the influence of southern origin water in both the surface and subsurface penetrates considerably north of the equator. As in the south, the northern high salinity waters have low normalized calcium, but these values may not be as low, nor are the salinities as high, as their southern counterpart and their southward extension appears to be cut off by fresher water from further north that is both upwelled and transported around the northern gyre.

## CONCLUSIONS

1) It appears, as suggested by SHILLER and GIESKES (1980), that for the surface and subsurface equatorial Pacific Ocean, circulation features and water "history" or "preformed" origins may play a more important role in the vertical distribution of calcium and alkalinity than local production-dissolution of  $\text{CaCO}_3$ .

2) The potential temperature-normalized surface calcium correlation of CHEN *et al.*, (1981) may not adequately model a "preformed" distribution for the calcium concentration of waters above  $20^\circ\text{C}$  in the equatorial Pacific due to their varied origin, yet presently similar temperature.

3) Waters immediately below the intermediate waters may have "preformed" values, with respect to the Pacific Ocean (not necessarily surface values) considerably lower in calcium while differing less noticeably in alkalinity.

4) As seen by others, biological utilization of calcium is probably greatest in the warm high-salinity waters of the tropics and subtropics. It would appear that long residence times in these waters leads to diminished normalized calcium values similar to the manner in which nutrient concentrations are kept very low.

5) The near-surface trans-equatorial distribution of calcium appears to largely reflect circulation features combined with "preformed" variation and presents a picture consistent with the findings of others for various chemical tracers in the "equatorial water mass".

6) Any further attempt to study these features would be better served by spacing stations no further apart than  $1^\circ$  in latitude.

There appear to be some reasonably sharp boundaries in the distribution of normalized calcium that this study has not properly resolved. Some effort also needs to be made to determine why the ranges reported of normalized calcium values (or Ca/Cl) vary so much between investigators, especially for samples from the high salinity waters of the subtropical gyres.

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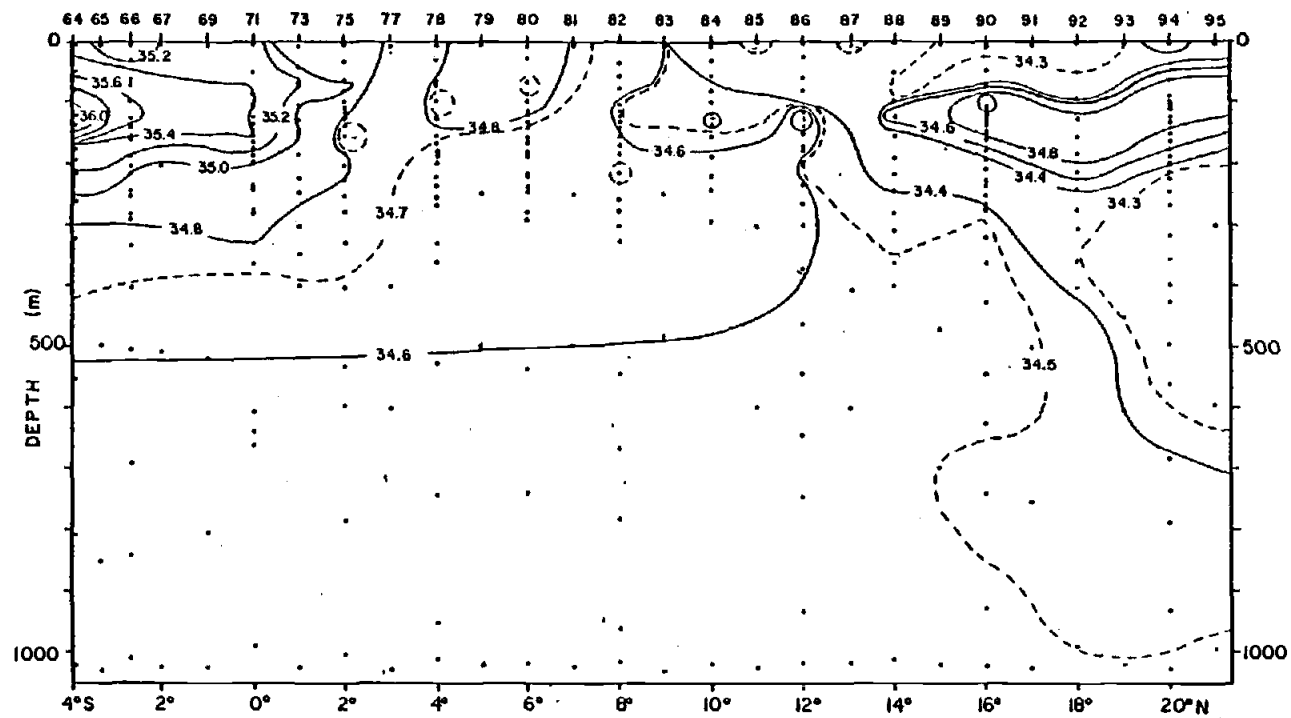


Fig. 1 Cross section of salinity from 4°S to 21°N along 158°W for leg 3.

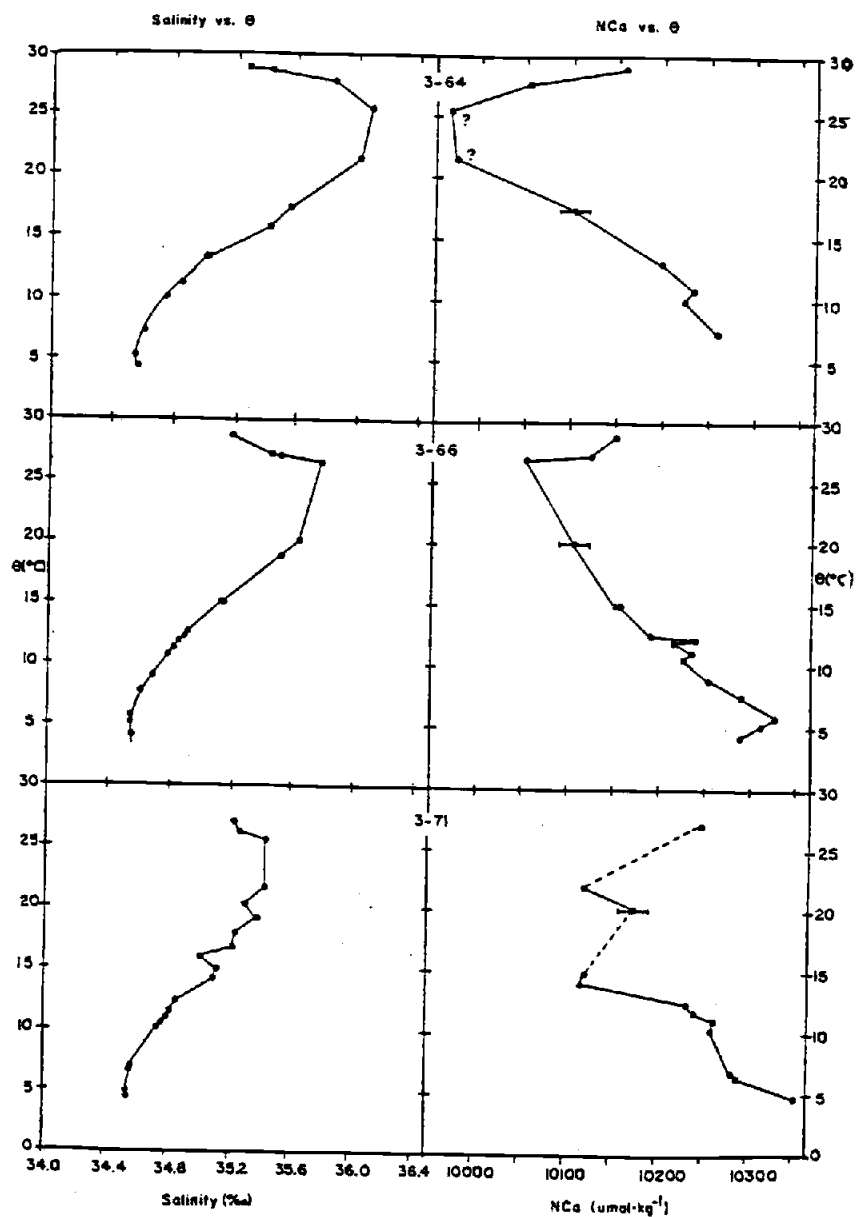


Fig. 2(a) Side-by-side comparisons of  $\theta$ -salinity and  $\theta$ -NCa for the samples of legs 3 and 13. The error bars approximate  $\pm 15 \text{ } \mu\text{mol kg}^{-1}$  ( $2\sigma$ ) in NCa.

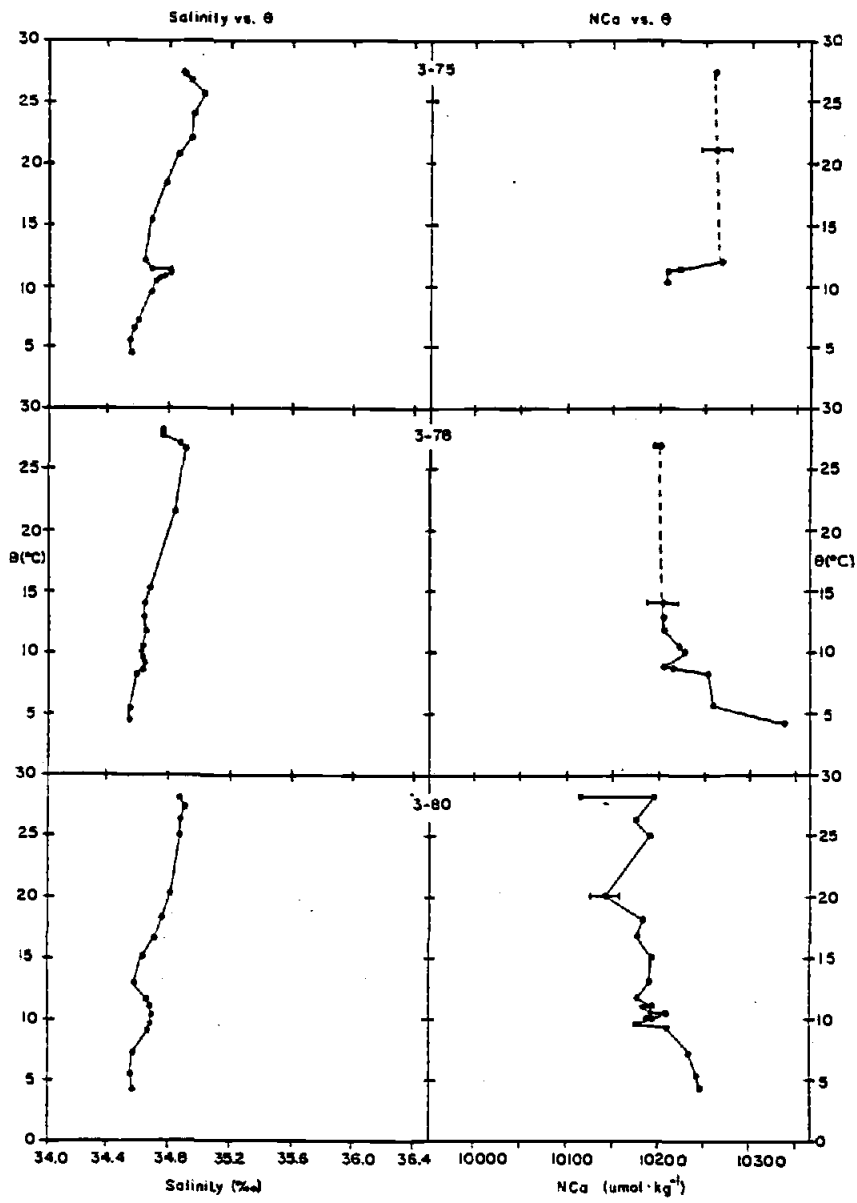


Fig. 2(b)

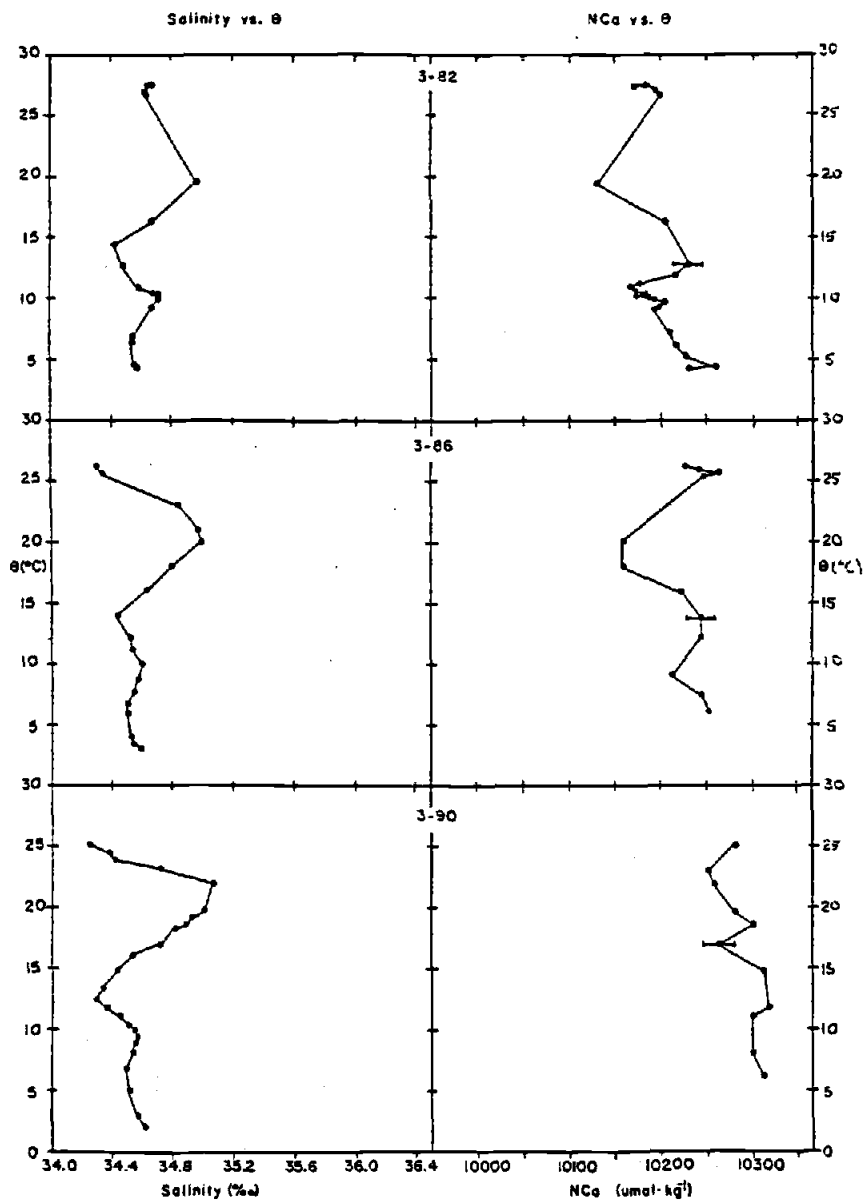


Fig. 2(c)

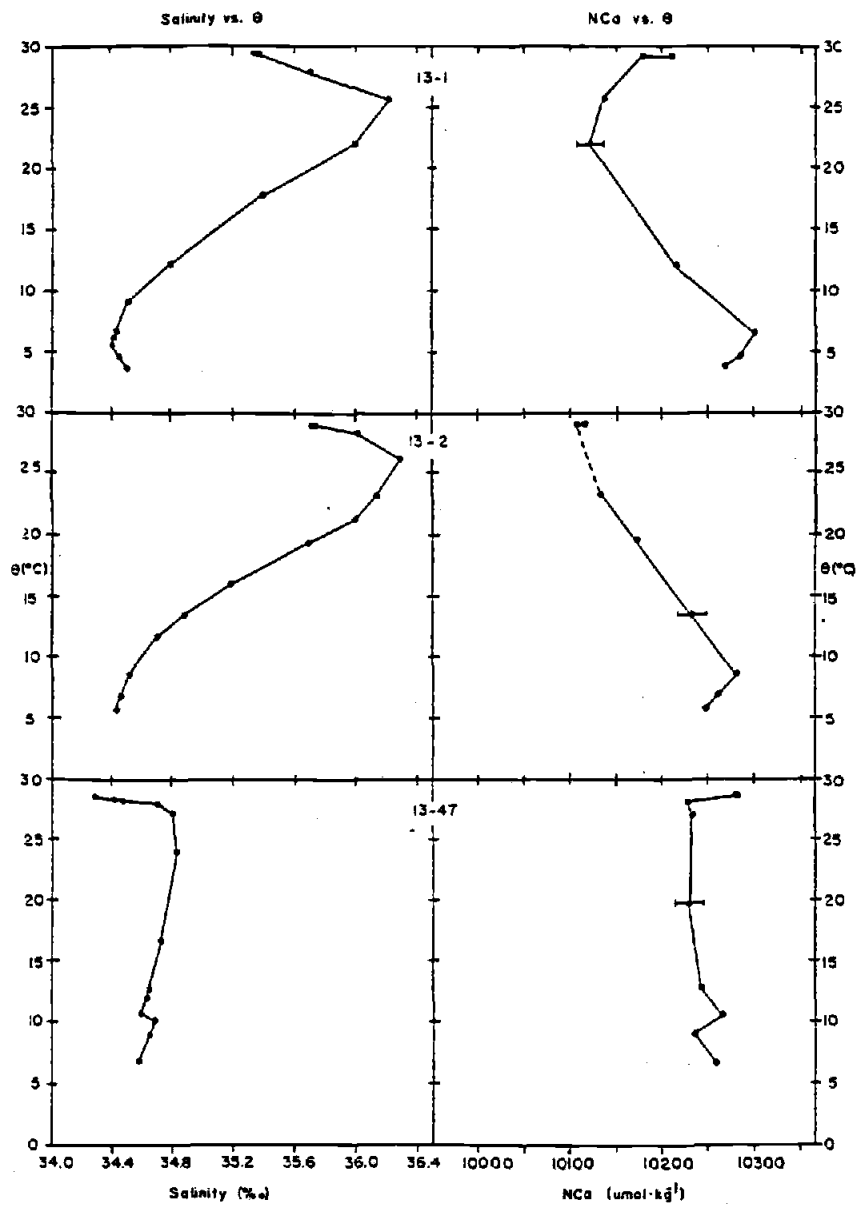


Fig. 2(d)

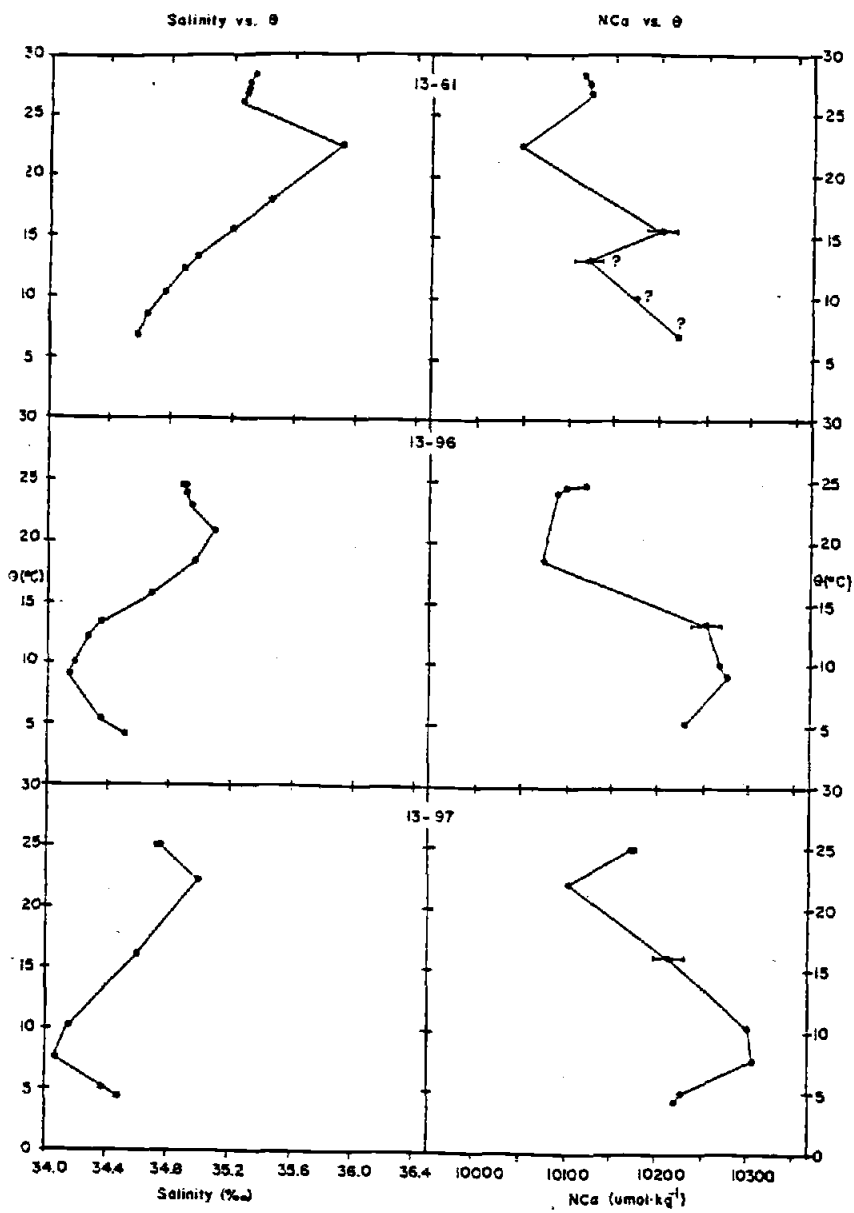


Fig. 2(e)

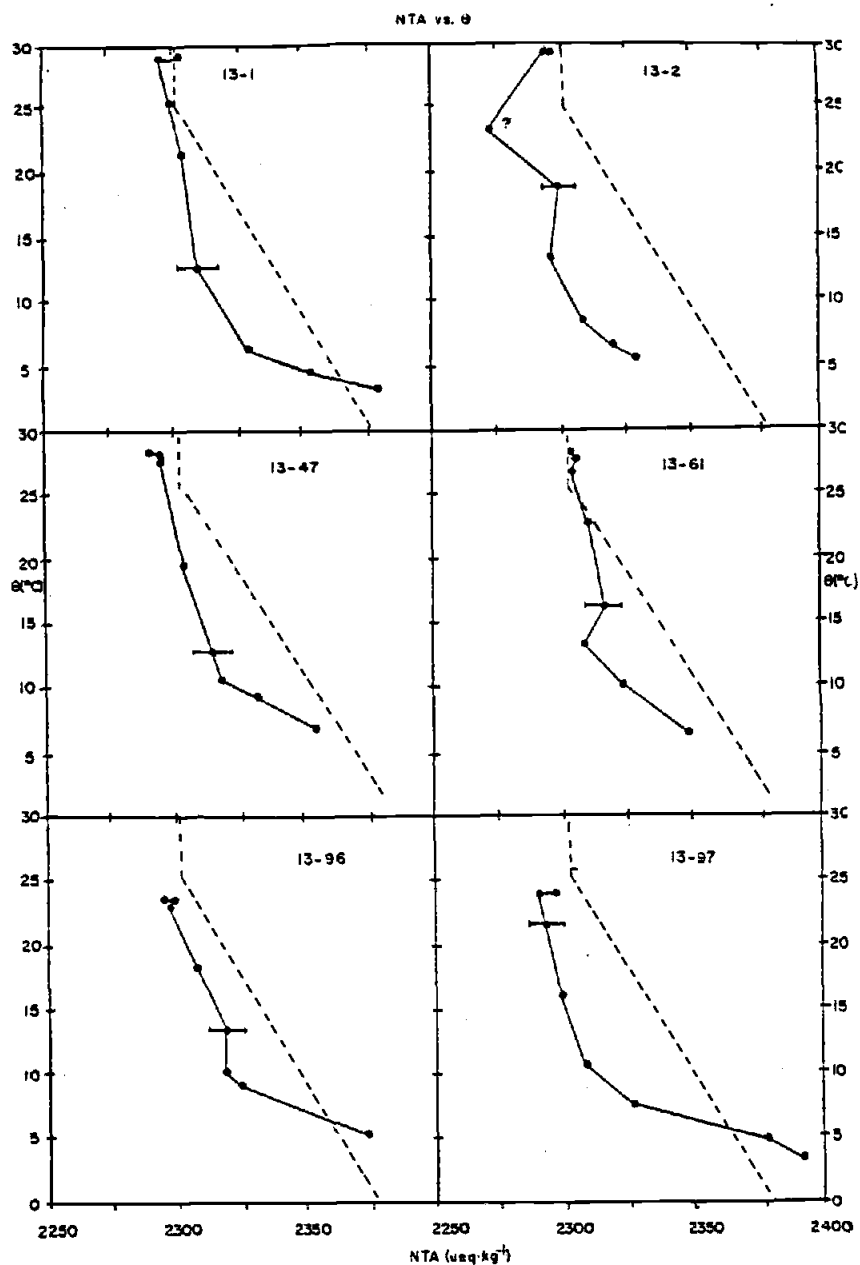


Fig. 3  $\theta$ -NTA diagrams for the six stations sampled in leg 13. The dashed lines represent "preformed" values calculated from the equations of CHEN and PYTKOWICZ (1979).

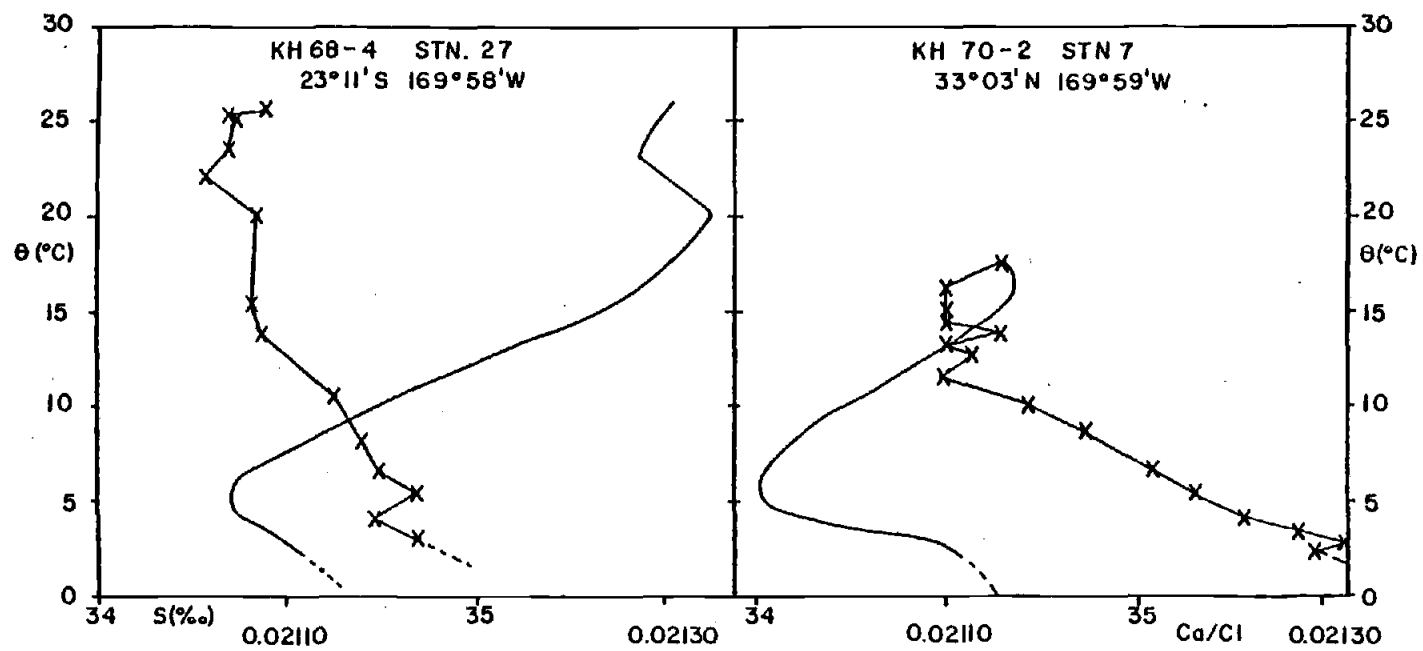


Fig. 4 Ca/Cl and salinity versus potential temperature (for the upper 1500 m) from the data of TSUNOGAI *et al.* (1973).



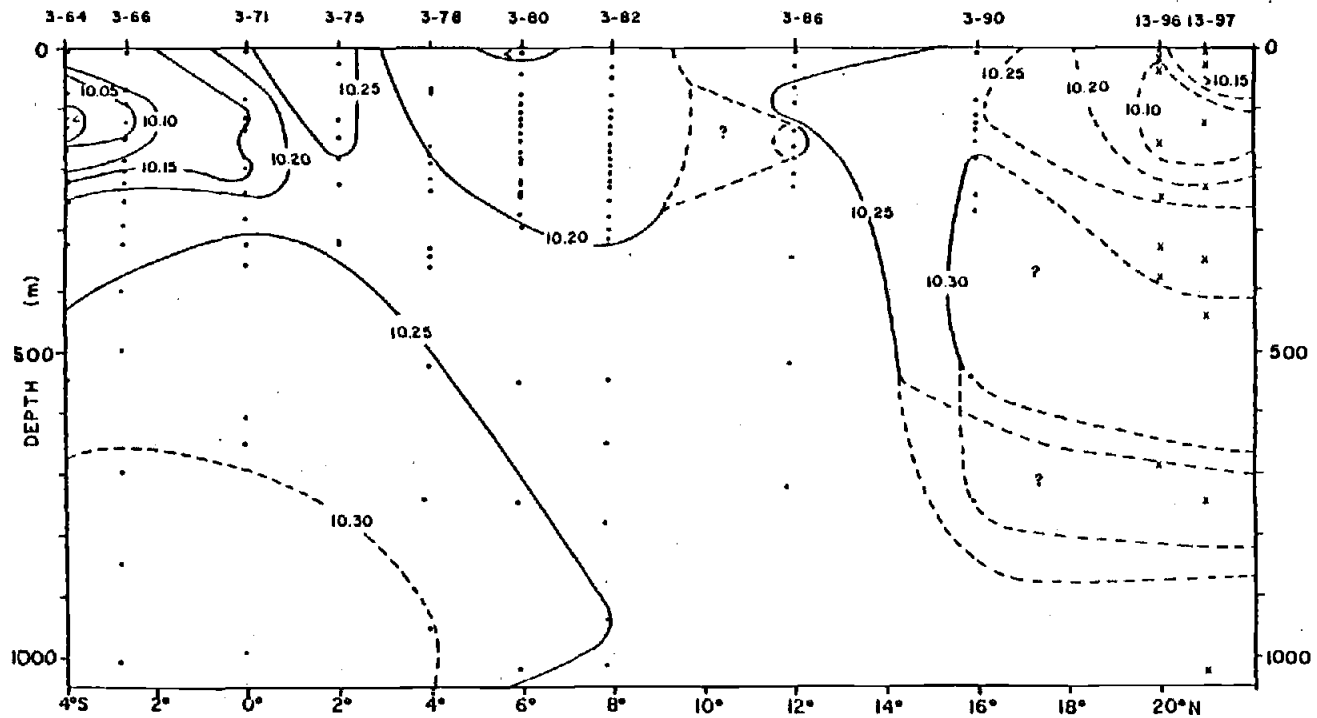


Fig. 5 Cross section of normalized calcium from 4°S to 21°N along 158°W for legs 3 and 13. The dashed lines indicate uncertainty due to both data sparsity and the difference in transect legs. Crosses represent data of leg 13.

## BIBLIOGRAPHY

- ALMGREN T., D. DYRSSEN and M. STRANDBERG (1977) Computerized high-precision titrations of some major constituents of seawater on board the R.V. *Dmitry Mendeleev*. *Deep-Sea Research*, 24, 345-364.
- ATWOOD D.K., P.N. FROELICH and W.F. KINARD (1973) Temporal and depth study of alkaline earth chlorinity ratios in seawater at a single station south of Puerto Rico. *Limnology and Oceanography*, 18, 771-783.
- BE A.W.H. (1960) Some observations on arctic planktonic foraminifera. *Contributions to the Cushman Foundation for Foraminiferal Research*, 11, 64-68.
- BILLINGS G.K., O.P. BRICKER, F.T. MACKENZIE and A.L. BROOKS (1969) Variation of alkaline earth element/chlorinity ratios in the Sargasso Sea. *Earth and Planetary Science Letters*, 6, 231-236.
- BREWER P.G. and A. BRADSHAW (1975) The effect of non-ideal composition of seawater on salinity and density. *Journal of Marine Research*, 33, 157-175.
- BREWER P.G., G.T.F. WONG, M.P. BACON and D.W. SPENCER (1975) An oceanic calcium problem? *Earth and Planetary Science Letters*, 26, 81-87.
- BREWER P.G. and J.C. GOLDMAN (1976) Alkalinity changes generated by phytoplankton growth. *Limnology and Oceanography*, 21, 108-117.
- BROECKER W.S. (1974) "NO", a conservative water mass tracer. *Earth and Planetary Science Letters*, 23, 100-107.
- BROECKER W.S. and H.G. OSTLUND (1979) Property distributions along the  $\sigma_\theta = 26.8$  isopycnal in the Atlantic Ocean. *Journal of Geophysical Research*, 84, 1145-1154.

- CHEN C.T. (1978) Decomposition of calcium carbonate and organic carbon in the deep oceans. *Science*, 201, 735-736.
- CHEN C.T. and R.M. PYTKOWICZ (1979) On the total CO<sub>2</sub>-titration alkalinity-oxygen system in the Pacific Ocean. *Nature*, 281, 362-365.
- CHEN C.T., R.M. PYTKOWICZ and E.J. OLSON (1981) Evaluation of the calcium problem in the South Pacific. *Geochemical Journal* ( in press).
- CULBERSON C.H., R.M. PYTKOWICZ and J.E. HAWLEY (1970) Seawater alkalinity determination by the pH method. *Journal of Marine Research*, 28, 15-21.
- CULBERSON C.H. and R.M. PYTKOWICZ (1973) Ionization of water in seawater. *Marine Chemistry*, 1, 309-316.
- CULKIN F. and R.A. COX (1966) Sodium, potassium, magnesium, calcium and strontium in seawater. *Deep-Sea Research*, 13, 789-804.
- DATE Y. and K. TOEI (1963) The selective titrations of calcium in the presence of magnesium. *Bulletin of the Chemical Society of Japan*, 36 518-521.
- DITTMAR W. (1884) Report on researches into the composition of ocean water collected by H.M.S. *Challenger* during the years 1873-1876. In: *The voyage of H.M.S. Challenger*, J. MURRAY, editor, H.M. Stationary Office, London 1.
- DYRSSEN D. (1977) The chemistry of plankton production and decomposition in seawater. In: *Oceanic sound scattering prediction*, N.R. ANDERSON and B.J. ZAHURANCE, editors, Plenum Press, pp. 65-84.
- EDMOND J.M., S.S. JACOBS, A.L. GORDON, A.W. MANTYLA and R.F. WEISS (1979) Water column anomalies in dissolved silica over opaline pelagic sediments and the origin of the deep silica maximum.

- Journal of Geophysical Research*, 84, 7809-7826.
- FINE R.A. and H.G. OSTLUND (1980) Exchange times in the Pacific Equatorial current system. *Earth and Planetary Science Letters*, 49, 447-452.
- FINE R.A., J.L. REID and H.G. OSTLUND (1981) Circulation of tritium in the Pacific Ocean. *Journal of Physical Oceanography*, 11, 3-14.
- GOLDSTEIN D. (1959) A new indicator for the complexometric determination of calcium. *Analytica Chimica Acta*, 21, 339-340.
- GOLDSTEIN D. and C. STARK-MAYER (1958) New specific test for calcium. *Analytica Chimica Acta*, 19, 437-439.
- HAWAII-TAHITI SHUTTLE PRELIMINARY HYDROGRAPHIC REPORT--LEG 13 (1980) Scripps Institute of Oceanography Preliminary Publication 198.
- HAWAII-TAHITI SHUTTLE EXPERIMENT--HYDROGRAPHIC DATA REPORT (1981) Volumes I-IV. Scripps Institute of Oceanography Reference Numbers 81-5 to 81-8.
- HORIBE Y., K. ENDO and H. TSUBOTA (1974) Calcium in the South Pacific and its correlation with carbonate alkalinity. *Earth and Planetary Science Letters*, 23, 136-140.
- INGLE S.E. (1973) Solubility of calcite in the ocean. *Marine Chemistry*, 3, 301-319.
- JAGNER D. (1974) High precision determination of calcium in the presence of higher concentrations of magnesium by means of a computerized photometric titration. Application to seawater. *Analytica Chimica Acta*, 68, 83-92.
- JOHNSON K.J. (1979) Ion association and activity coefficients in electrolyte solutions. Ph.D. Dissertation, Oregon State University, 335 pp.

- JOHNSON K.J., R. VOLL, C.A. CURTIS and R.M. PYTKOWICZ (1977) A critical examination of the NBS pH scale and the determination of titration alkalinity. *Deep-Sea Research*, 24, 915-926.
- KANAMORI S. and H. IKEGAMI (1980) Computer-processed potentiometric titration for the determination of calcium and magnesium in seawater. *Journal of the Oceanographical Society of Japan*, 36, 177-184.
- KEELING C.D. and B. BOLIN (1968) The simultaneous use of chemical tracers in oceanic studies. *Tellus*, 20, 17-54.
- KESTER D.R. (1974) Marine chemical equilibria and kinetics. In: *The oceans handbook*, R.A. HORNE, editor, in press.
- KRUMGALZ D. and R. HOLZER (1980) On the determination of  $\text{Ca}^{2+}$  ion concentration in seawater. *Limnology and Oceanography*, 25, 367-370.
- LEBEL J. and A. POISSON (1976) Potentiometric determination of calcium and magnesium in seawater. *Marine Chemistry*, 4, 321-332.
- LISITZIN A.P. (1972) Sedimentation in the World Ocean. *Special Publications of the Society of Economic Paleontologists and Mineralogists*, 17, 218 pp.
- MCINTYRE A., A.W.H. BE and M.B. ROCHE (1970) Modern Pacific coccolithophorids: a paleontological thermometer. *Transactions of the New York Academy of Science*, 32, 720-731.
- MONTGOMERY R.B. (1979) Salinity and the residence time of subtropical oceanic surface water. In: *The atmosphere and the sea in motion*, B. BOLIN, editor, Rockefeller Institute Press and Oxford University Press, pp. 143-146.
- REID J.L. (1965) *The intermediate waters of the Pacific Ocean*, Johns Hopkins Oceanographic Studies, Number 2, 85 pp.
- REID J.L. (1973) The shallow salinity minimum of the Pacific Ocean.

- Deep-Sea Research*, 20, 51-68.
- RILEY J.P. (1975) Analytical chemistry of seawater. In: *Chemical oceanography*, J.P. RILEY and G. SKIRROW, editors, Academic Press, 3, pp. 193-514.
- RILEY J.P. and M. TONGUDAI (1967) The major cation/chlorinity ratios in seawater. *Chemical Geology*, 2, 263-269.
- RINGBOM A., G. PENSAR and E. WANNINEN (1958) A complexometric titration method for determining calcium in the presence of magnesium. *Analytica Chimica Acta*, 19, 525-531.
- SADEK F.S., R.W. SCHMID and C.N. REILLEY (1959) Visual EGTA titration of calcium in the presence of magnesium. *Talanta*, 2, 38-51.
- SAGI T. (1969) The concentration of calcium and the calcium/chlorosity ratio in the western North Pacific Ocean. *Oceanographical Magazine*, 21, 61-66.
- SCHMID R.W. and C.N. REILLEY (1957) New complexon for titration of calcium in the presence of magnesium. *Analytical Chemistry*, 29, 264-268.
- SCHWARZENBACH G. and H. FLASCHKA (1969) *Complexometric titrations*, Methuen, 490 pp.
- SHILLER A.M. and J.M. GIESKES (1980) Processes affecting the oceanic distributions of dissolved calcium and alkalinity. *Journal of Geophysical Research*, 85, 2719-2727.
- SVERDRUP H.U., M.W. JOHNSON and R.H. FLEMING (1942) *The oceans: their physics, chemistry and general biology*. Prentice-Hall, 1087 pp.
- TAFT B.A. and P. KOVALA (1979) Temperature, salinity, thermohaline anomaly and zonal geostrophic velocity sections along 150°W from NORPAX Shuttle Experiment (1977-1978). Department of Oceanography

- Special Report Number 87, Reference M79-17, University of Washington, 28 pp.
- TAKAHASHI T., W.S. BROECKER, A.E. BAINBRIDGE and R.F. WEISS (1980) Carbonate chemistry of the Atlantic, Pacific and Indian Oceans: The results of the GEOSECS expeditions 1972-1978. Lamont-Doherty Geological Observatory, Technical Report, CU-1-80.
- THOMPSON T.G. and C.C. WRIGHT (1930) Ionic ratios in the waters of the North Pacific Ocean. *Journal of the American Chemical Society*, 52,915-921.
- TRAGANZA E.D. and B.J. SZABO (1967) Calculation of calcium anomalies on the Great Bahama Bank from alkalinity and chlorinity data. *Limnology and Oceanography*, 12,281-286.
- TSUCHIYA M. (1968) *Upper waters of the intertropical Pacific Ocean*. Johns Hopkins Oceanographic Studies, Number 4, 50 pp.
- TSUNOGAI S., M. NISHIMURA and S. NAKAYA (1968a) Complexometric titration of calcium in the presence of larger amounts of magnesium. *Talanta*, 15,385-390.
- TSUNOGAI S., M. NISHIMURA and S. NAKAYA (1968b) Calcium and magnesium in seawater and the ratio of calcium to chlorinity as a tracer of water masses. *Journal of the Oceanographical Society of Japan*, 24, 153-159.
- TSUNOGAI S., T. YAMAZAKI and M. NISHIMURA (1971) Calcium in the Antarctic Ocean. *Journal of the Oceanographical Society of Japan*, 27,191-196.
- TSUNOGAI S., H. YAMAHATA, S. KUDO and O. SAITO (1973) Calcium in the Pacific Ocean. *Deep-Sea Research*, 20,717-726.

WANNINEN E. (1961) Selection of complexing agents for complexometric titrations. *Talanta*, 8, 335-363.

WATTENBERG H. (1933) Das Chemische Beobachtungs-Material und Seine Gewinnung. Kalzium-Karbonat und Kohlensaurgehalt des Meerwassers. Deutsches Atlantischen Expedition "Meteor" 1925-1927. Cited from TRAGANZA and SZABO, 1967.

WYRTKI K., E. FIRING, D. HALPERN, R. KNOX, G.J. MCNALLY, W.C. PATZERT, E.D. STROUP, B.A. TAFT and R. WILLIAMS (1981) The Hawaii to Tahiti Shuttle Experiment. *Science*, 211, 22-28.



APPENDICES

## APPENDIX I

The paper presented as Chapter 2 provides the background information for the procedure used and the results of the investigation into interference effects of other alkaline earth elements on the EGTA titration of calcium. That work and most of the work cited took the empirical approach to the interference problem but some mention was made of the theoretical evaluation of the titration using titrant-ion stability constants and the "conditional" constants that result under non-ideal conditions. This section is devoted to a more detailed evaluation of the theoretical approach which may provide a better understanding of both the interference effects and the titration theory itself.

A preliminary examination of the stability constants for EGTA-cation complexes ( $10^{11}$ ,  $10^{8.5}$ , and  $10^{5.2}$  for Ca, Sr, and Mg respectively; Schwarzenbach and Flaschka, 1969) reveals that strontium could interfere, though its concentration in seawater is only about 1% that of calcium. For seawater, it is more acceptable to evaluate the "conditional" or "effective" stability constants for this titration under several different conditions and to construct the theoretical titration curves (Schwarzenbach and Flaschka, 1969).

The stability constant for a cation (M)-chelate (Z) complex (MZ) is

$$K_{MZ} = \frac{[MZ]}{[M][Z]} \quad (1)$$

However, under non-ideal conditions, in the presence of competitive ions for cation and chelator, the "conditional" constant is used in theoretical evaluations of complexometric titration curves. The con-

ditional constant is defined as

$$K'_{MZ} = \frac{[MZ]}{[M'] [Z']} \quad (2)$$

where  $[M']$  is the concentration of a cation not complexed by the titrant regardless of what other form it takes and  $[Z']$  is similarly the concentration of chelator not complexed by the cation regardless of what other form it takes.

Another form of expressing the conditional constant is

$$K'_{MZ} = \frac{K_{MZ}}{\alpha_M \alpha_Z} \quad (3)$$

where

$$\alpha_M = \frac{[M']}{[M]} = 1 + \sum [L] K_{ML} \quad (4)$$

$$\alpha_Z = \frac{[Z']}{[Z]} = 1 + \sum [N] K_{ZN} \quad (5)$$

L is a ligand other than the chelator and N is a complexing cation other than the one of interest.

Using equation (2) and the following two definitions with subscript t defined as total (regardless of form) concentration,

$$[M]_t = [M'] + [MZ] \quad (6)$$

$$[Z]_t = [Z'] + [MZ] \quad (7)$$

and the definition as the fraction of equivalence  $\underline{a}$  equal to  $\frac{[Z]_t}{[M]_t}$ , one can derive an expression for  $[M']$  in terms of  $K'$ ,  $[M]_t$ , and  $\underline{a}$ ;

$$K' [M']^2 - [M'] (K' [M]_t - K' [M]_t \underline{a} - 1) - [M]_t = 0 \quad (8)$$

For any particular condition of  $K'$  and  $[M]_t$ , one can calculate  $[M']$  or  $pM'$  as a function of  $\underline{a}$ .

As a first example  $K'$  will be taken as  $10^{11}$ , the value for the EGTA-Ca stability constant, implying no interference of any kind, and  $[M]_t$  will be taken as  $0.0104 \text{ M}$  which is a value approximating the calcium concentration of 35 ‰ seawater. As the titration is done here, the solution volume approximately doubles with complete addition of titrant. Therefore,  $[M]_t$  is multiplied by  $\frac{1}{1+a}$  as the curve is determined (reagent volumes and wash down water are ignored here). Curve i from Fig. 6 is the resulting plot of  $pM'$  vs.  $a$  for these conditions. Clearly there is a sharp jump in  $pM'$  at the theoretical equivalence point resulting in a large difference in calcium concentration before and after the region of equivalence ( $a$  near 1.0) and leaving untitrated only  $2.3 \times 10^{-7}$  mole/l at  $a = 1.00$ . With the final volume being approximately double the sample aliquot this amount of calcium is about 0.004% of the original. If the indicator undergoes its color change in this region of large  $pM'$  jump (nearly 5 orders of magnitude in concentration) then the titration endpoint will be essentially identical to the equivalence point and should give a very accurate value (at the  $\mu\text{M}$  level).

One of the several possible interferences which must be taken into account is that of the protons in solution with the titrant. If the initial pH of the seawater sample is approximately 8.0, then  $\alpha Z(H) \approx 234$  ( $\log K_1 = 9.46$ ,  $\log K_2 = 8.85$ ,  $\log K_3 = 2.68$ , and  $\log K_4 = 2.00$  for  $H_{1-4}$ -EGTA, Schwarzenbach and Flaschka, 1969). This value of  $\alpha Z(H)$  results in  $K'$  being approximately two orders of magnitude lower, which in turn results in a smaller  $pM'$  jump and more calcium untitrated at the theoretical equivalence point. However, as the titration is done here, a high pH buffer ( $\approx 12.3$ ) is used in the final 2% of the titra-

tion and  $\alpha Z(H)$  becomes approximately 1 at such a low hydrogen ion concentration. The result is titration curve ii using the reduced  $K'$  for the first 98% (up to  $\underline{a} = 0.98$ ) of the titration and  $K$  for the last 2%. The curve is essentially identical to curve i. It is also important to remember that this interference would reduce  $K'$  for each titration-cation (EGTA-Ca, Mg or Sr) combination equally, and therefore have no effect on the relative interferences of the cations upon each other.

Interference of another kind involves complexing of the cation(s) of interest by species in solution other than the titrant. In the titration of seawater this type of interference could occur because of the ion-pair complexes that form with calcium, magnesium and strontium. A quick examination of the various stability constant-concentration products that would make up a cation-ion pair reveals that there is no combination of  $K_{ML} \times [L]$  that is much greater than 1 (values of ion-pair stability constants for Ca, Mg, and Sr from Kester, 1974; Johnson, 1979). Even at the high pH portion of the titration the ion pair complexing of calcium is insignificant relative to the calcium-titrant stability. This is not true for the magnesium in solution because it precipitates (presumably as the hydroxide) upon addition of the high pH buffer. Precipitation actually reduces the interference of magnesium (via competition for EGTA) on the titration of calcium by reducing  $K'$  EGTA-Mg tremendously. However, as it will be shown in the next section, the competitive interference of magnesium is less than that of strontium.

With pH effects and ion-pair effects both relatively insignificant, an interference that remains to be accounted for is that of the alkaline earth cations upon each other. Using values of  $K$  of  $10^{11}$ ,  $10^{8.5}$ , and  $10^{5.2}$  for Ca, Sr, and Mg respectively and respective concentrations

of 0.01 M, 0.09 mM, and 0.05 M (approximating 35 ‰ seawater concentrations) the following K's can be calculated:

$$\log K'_{\text{Ca-EGTA}}, \text{ Mg interference} = 7.10$$

$$\log K'_{\text{Ca-EGTA}}, \text{ Sr interference} = 6.54$$

$$\log K'_{\text{Ca-EGTA}}, \text{ Mg + Sr interference} = 6.44$$

$$\log K'_{\text{Mg-EGTA}}, \text{ Ca + Sr interference} = -3.80$$

$$\log K'_{\text{Sr-EGTA}}, \text{ Ca + Mg interference} = -0.50$$

Clearly the presence of strontium at seawater concentration has a greater effect than magnesium on the calculated stability constants, but these calculations would seem to indicate that there is still sufficient separation in the effective stability constants for successful titration of calcium to take place.

Using  $K'_{\text{Ca-EGTA}}$ , Mg + Sr interference in equation (8) with the same  $[M]_t$  titration curve iii is produced. The jump in  $pM'$  is much less and the untitrated calcium at the equivalence point is  $4.4 \times 10^{-5}$  mole/l which corresponds to about 0.88% of the original amount. It should be stressed again that the theoretical equivalence point is not necessarily the point at which the indicator completes its color change. The indicator may still be sensitive enough to indicate this amount of calcium and the titration would continue past  $\underline{a} = 1.00$ .

The last adjustment to the theoretical calculation that will be considered is to account for the change in conditions at  $\underline{a} = 0.98$  in the titration. The volume of solution is doubled and approximately 98% of the necessary titrant is added in one step. Besides titrating

the calcium in solution, this doubling of volume effectively dilutes the interfering strontium. With the addition of indicator, buffer, and extractant, the magnesium falls out of solution and  $K'$  Ca-EGTA becomes

$$K' \text{ Ca-EGTA} = \frac{10^{11}}{(1)(1 + 10^{8.5} \times 4.5 \times 10^{-5})}$$

$$\log K' = 6.85$$

Titration curve iv showing slightly improved features is the result. The calcium remaining untitrated at  $a = 1.00$  is  $2.7 \times 10^{-5}$  mole/l or approximately 0.52% of the original amount.

While these theoretical titration curves are useful in the sense that they demonstrate the effects of ions which interfere, on both the degree of  $pM'$  increase and the associated equivalence point concentration, they do not give the true measure of this titration's accuracy. As mentioned several times previously, it is indicator sensitivity to calcium that determines when the titration "end-point" is achieved. If the indicator gives its end-point indication in the region of sharp  $pM'$  increase (as a properly selected indicator should), then the larger the jump in  $pM'$  and/or the less the equivalence point concentration of calcium, then the more accurately will the end-point be determined for a given indicator sensitivity. If, however, the indicator still shows the presence of calcium beyond the equivalence point, as might be the case in curves iii and iv, the apparent titration error swings from negative (the untitrated calcium at the equivalence point) to positive. This is because excess titrant (more than 1 mole titrant per mole calcium) is necessary to reduce the calcium concentration beyond the equivalence point. This titration-indication scheme could

be theoretically evaluated much as the EGTA-zinc-zincon (Sadek et al., 1959; Wanninen, 1961; Jagner, 1974) has been if more information were available. Stability constants for indicator complexes with the cations of interest and with interferents (including  $H^+$ ) would be necessary to make this a proper evaluation. Additionally, the alcoholic extraction undoubtedly has an effect on all  $K'$  values involved. While the vigorous stirring employed makes it a reasonable assumption that most of the interaction takes place in the aqueous phase, each pause for observation involved concentration of the untitrated calcium into a small volume of alcohol containing a relatively large amount of indicator. The precipitation of magnesium (presumably as the hydroxide) also lends the possibility of co-precipitation and/or occlusion of calcium, though ideally, the bulk titrant addition prior to precipitation minimizes such an effect. There is some difference then between a theoretical titration and that observed using this particular procedure. Therefore, the empirical approach taken in Chapter 2 is the most practical way to evaluate correction factors.



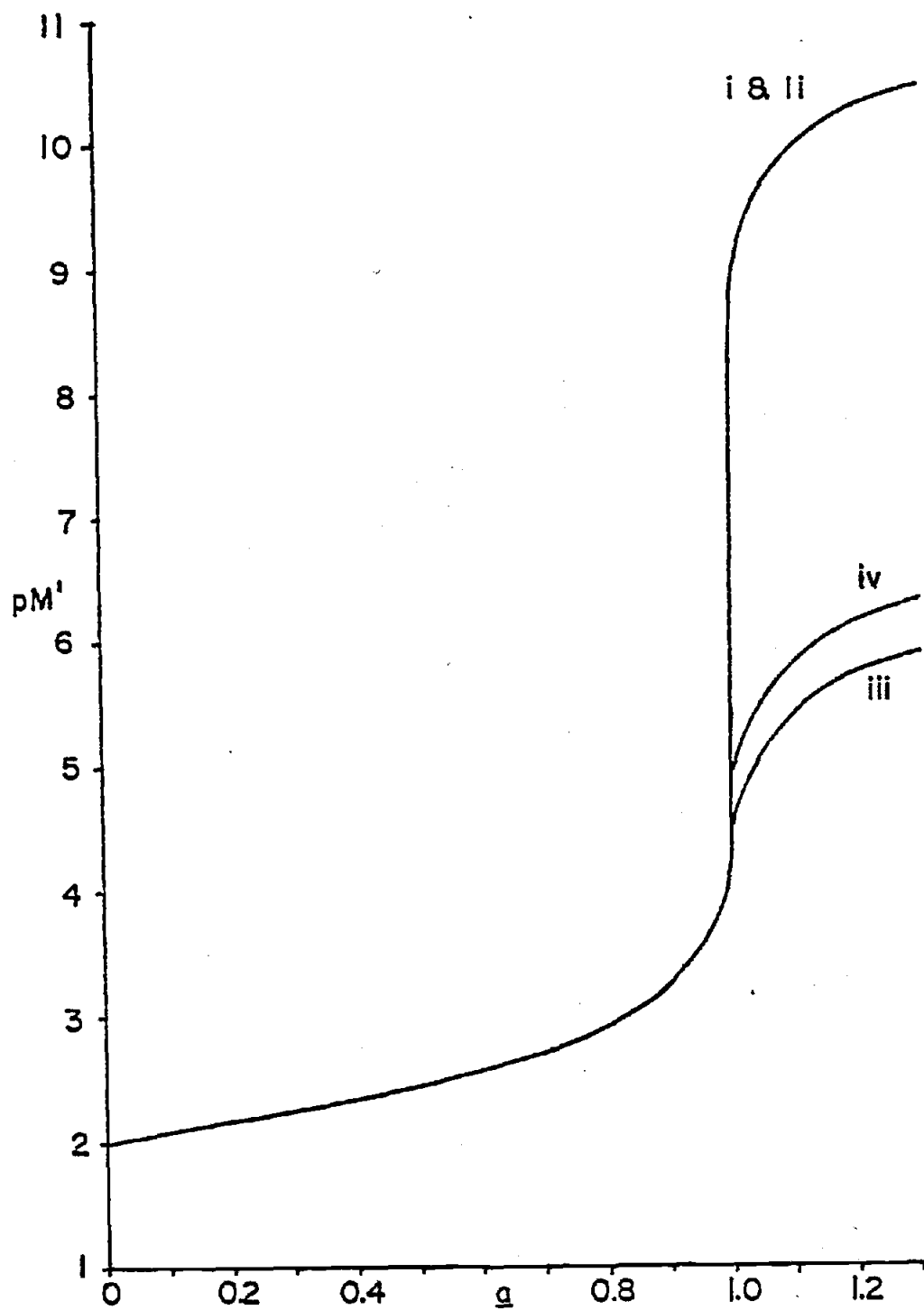


Fig. 6  $pM'$  versus fraction of titration equivalence ( $a$ ) for various calcium-EGTA association constants.

## APPENDIX II

The following tables contain the data used in the manuscript written up as Chapter 3 of this thesis. The stations are identified by the shuttle leg number and station number and the station position and date occupied are also listed. The hydrographic data of depth, potential temperature and salinity are from the respective hydrographic reports as noted in Chapter 3. The single exception to this is station 97 of leg 13 for which the hydrographic data was obtained from the Hawaii-Tahiti Shuttle Preliminary Hydrographic Data Report (1980).

The remainder of data listed is as follows:

Ca ( $\mu\text{mol/kg}$ ) = The calcium concentration of the original water samples.

NCa ( $\mu\text{mol/kg}$ ) = The calcium concentration of the sample normalized to 35 ‰ salinity.

TA ( $\mu\text{eq/kg}$ ) = The alkalinity of the original water sample.

NTA ( $\mu\text{eq/kg}$ ) = The alkalinity of the sample normalized to 35 ‰ salinity.

Normalization was calculated as in the following example,

$$\text{NCa } (\mu\text{mol/kg}) = \frac{\text{Ca } (\mu\text{mol/kg})}{\text{Sal. (ppt)}} \times 35 \text{ ppt}$$

The asterisk appearing under samples from leg 13 represents duplicate analyses and the resulting NCa value determined approximately one year after the first analyses.

## Station 3-64 4°S, 158°W 22 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
5	28.95	35.270	10233	10156	2276	2259
81	27.87	35.430	10291	10050	2314	2261
123	25.57	36.078	10272	9967	2306	2237
149	21.44	35.997	10257	9972	2332	2267
174	17.27	35.364	10202	10099	2295	2272
221	13.18	34.997	10192	10195	2263	2264
268	11.29	34.848	10189	10233	2262	2272
326	10.00	34.754	10145	10219	2260	2276
547	7.23	34.592	10138	10257	2262	2288

## Station 3-66 2°30'S, 158°W 23 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
6	28.61	35.189	10205	10151	2281	2269
67	27.33	35.456	10250	10117	2296	2267
95	26.91	35.783	10281	10054	2315	2265
125	20.15	35.637	10289	10103	2306	2265
163	15.13	35.143	10195	10151	2270	2260
166	14.98	35.167	10203	10156	2265	2254
187	12.69	34.921	10165	10190	2265	2270
206	12.44	34.900	10210	10238	2253	2259
216	12.17	34.885	10182	10214	2268	2275
255	11.55	34.843	10181	10228	2268	2278
292	11.23	34.823	10180	10233	2268	2280
337	10.66	34.792	10163	10224	2250	2263
405	8.89	34.683	10162	10253	2268	2289
506	7.60	34.608	10174	10291	2254	2280
690	5.87	34.546	10192	10325	2292	2322
845	5.17	34.544	10178	10311	2288	2319
1012	4.28	34.555	10157	10286	2309	2339

## Station 3-71 0°N, 158°W 24 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
4	26.97	35.233	10315	10248	2292	2276
85	25.38	35.442	10324	10195	2303	2274
103	21.63	35.422	10244	10122	2306	2279
124	20.20	35.297	10258	10170	2292	2273
187	14.90	35.131	10160	10122	2285	2276
200	14.09	35.017	10124	10117	2290	2289
241	12.37	34.868	10198	10238	2284	2293
280	11.78	34.839	10196	10243	2269	2279
331	11.04	34.797	10202	10262	2282	2296
366	10.23	34.736	10180	10257	2261	2278
602	6.68	34.570	10155	10282	2276	2305
659	6.31	34.558	10160	10291	2297	2326
993	4.48	34.552	10223	10354	2308	2338

## Station 3-75 2°N, 158°W 25 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
36	27.43	34.919	10238	10262	2238	2243
119	20.94	34.864	10221	10262	2248	2257
157	12.07	34.644	10162	10267	2244	2267
186	11.51	34.810	10165	10219	2252	2264
225	11.29	34.805	10156	10214	2251	2263
330	10.30	34.710	10130	10214	2254	2273

## Station 3-78 4°N, 158°W 26 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
72	27.09	34.875	10158	10195	2257	2265
72	27.22	34.875	10163	10199	2259	2267
166	14.05	34.644	10102	10204	2238	2261
183	12.88	34.641	10100	10204	2249	2273
197	11.80	34.651	10104	10204	2265	2288
221	10.45	34.625	10111	10219	2252	2276
238	10.15	34.617	10118	10228	2233	2258
334	8.73	34.636	10101	10204	2268	2292
362	8.52	34.635	10107	10214	2271	2295
529	7.14	34.581	10131	10253	2277	2305
742	5.55	34.548	10124	10257	2300	2331
953	4.58	34.553	10204	10334	2329	2360

## Station 3-80 6°N, 158°W 27 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
6	27.98	34.882	10077	10112	2298	2306
39	27.84	34.896	10162	10195	2289	2296
84	26.37	34.871	10139	10175	2288	2296
102	24.96	34.868	10144	10185	2289	2298
118	20.19	34.818	10088	10141	2290	2302
124	18.34	34.754	10107	10180	2292	2308
138	16.74	34.710	10090	10175	2291	2310
142	15.16	34.634	10088	10195	2281	2306
158	13.01	34.582	10068	10190	2278	2305
166	11.68	34.648	10073	10176	2282	2305
190	10.90	34.687	10104	10195	2300	2321
194	10.88	34.684	10089	10180	2299	2320
220	10.35	34.691	10104	10195	2301	2322
241	9.97	34.687	10095	10185	2304	2325
250	10.05	34.687	10098	10190	2301	2322
280	9.61	34.684	10085	10175	2318	2339
296	9.48	34.675	10115	10209	2323	2344
540	7.26	34.582	10113	10233	2323	2352
742	5.43	34.548	10109	10243	2358	2388
1021	4.28	34.565	10122	10248	2368	2398



## Station 3-82 8°N, 158°W 27 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
5	27.38	34.671	10074	10170	2269	2290
36	27.34	34.658	10078	10180	2281	2304
58	26.99	34.632	10088	10195	2267	2291
80	26.87	34.609	10088	10199	2251	2277
105	19.51	34.976	10123	10127	2281	2282
114	16.32	34.671	10109	10204	2291	2313
133	12.80	34.489	10079	10228	2292	2326
144	11.89	34.592	10093	10214	2293	2321
159	11.32	34.622	10069	10180	2298	2323
174	11.09	34.658	10065	10166	2308	2331
189	10.65	34.685	10080	10170	2304	2325
203	10.55	34.707	10095	10180	2313	2333
218	10.31	34.698	10085	10170	2302	2322
237	10.15	34.698	10097	10185	2306	2326
258	9.96	34.688	10100	10190	2301	2322
280	9.74	34.682	10111	10204	2313	2335
307	9.52	34.673	10102	10199	2307	2329
326	9.31	34.665	10098	10195	2304	2326
546	7.12	34.563	10081	10209	2336	2366
669	6.26	34.538	10081	10214	2341	2372
789	5.27	34.545	10090	10224	2355	2386
963	4.42	34.555	10126	10257	2373	2403
1017	4.34	34.558	10101	10228	2379	2409

## Station 3-86 12°N, 158°W 29 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
6	26.32	34.311	10034	10224	2228	2273
30	25.91	34.347	10055	10243	2236	2279
61	25.61	34.349	10074	10262	2232	2275
91	25.33	34.351	10057	10248	2226	2269
133	20.12	34.988	10153	10156	2285	2286
154	18.08	34.789	10100	10156	2271	2285
174	16.00	34.634	10114	10219	2262	2286
203	13.76	34.418	10031	10224	2250	2288
229	12.23	34.488	10076	10224	2264	2298
374	9.19	34.606	10097	10209	2300	2326
544	7.47	34.549	10091	10224	2314	2343
744	5.93	34.513	10089	10228	2333	2366

## Station 3-90 16°N, 158°W 30 April 1979

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )
6	25.02	34.242	10056	10277
86	23.09	34.721	10169	10253
112	21.93	34.974	10248	10257
130	19.59	34.990	10272	10277
146	18.65	34.891	10270	10301
163	16.81	34.705	10175	10262
183	14.76	34.432	10142	10311
242	11.82	34.370	10128	10315
272	10.95	34.461	10144	10301
547	8.01	34.546	10168	10301
741	6.11	34.494	10164	10311

## Station 13-1 17°S, 150°W 18 March 1980

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
7	29.17	35.422	10333	10209	2329	2302
16	29.17	35.428	10298	10175	2324	2296
101	25.57	36.214	10483	10132	2380	2300
201	21.74	35.985	10408	10122	2369	2304
399	12.42	34.787	10153	10214	2295	2309
595	6.56	34.417	10127	10301	2291	2329
838	4.62	34.447	10122	10286	2320	2356
1003	3.73	34.501	10122	10267	2345	2379

## Station 13-2 16°S, 150°W 18 March 1980

2	28.95	35.712	10320	10112	2343	2296
*				(10117)		
12	28.95	35.713	10304	10097	2340	2294
*				(10112)		
151	23.20	36.124	10456	10132	2345	2273
251	19.32	35.665	10362	10170	2343	2300
350	13.35	34.872	10160	10199	2288	2296
498	8.50	34.508	10138	10282	2274	2307
*				(10277)		
595	6.75	34.446	10096	10257	2284	2321
693	5.74	34.433	10083	10248	2291	2329

## Station 13-47 4°N, 153°W 29 March 1980

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca (umol/kg)	NCa (umol/kg)	TA (ueq/kg)	NTA (ueq/kg)
2	28.46	34.283	10065	10277	2243	2290
29	28.15	34.457	10070	10228	2259	2295
84	27.17	34.795	10192	10253	2281	2295
*				(10233)		
134	19.81	34.787	10168	10228	2291	2305
174	12.87	34.638	10138	10243	2289	2313
223	10.53	34.595	10147	10267	2289	2316
349	9.12	34.651	10129	10233	2308	2332
*				(10233)		
591	6.80	34.566	10131	10257	2326	2355

## Station 13-61 4°S, 153°W 1 April 1980

2	28.26	35.315	10203	10112	2325	2304
*				(10112)		
62	27.62	35.286	10198	10117	2325	2306
*				(10108)		
116	26.56	35.281	10202	10122	2324	2305
*				(10117)		
147	22.64	35.914	10308	10045	2371	2311
*				(10045)		
178	15.62	35.188	10259	10204	2330	2317
*				(10199)		
203	13.24	34.960	10108	10117	2306	2309
*				(10117)		
389	10.22	34.751	10104	10175	2307	2324
*				(10166)		
615	6.87	34.566	10085	10214	2321	2355
*				(10204)		

## Station 13-96 20°N, 158°W 10 April 1980

Depth (m)	Pot. Temp. (°C)	Sal. (ppt)	Ca ( $\mu\text{mol/kg}$ )	NCa ( $\mu\text{mol/kg}$ )	TA ( $\mu\text{eq/kg}$ )	NTA ( $\mu\text{eq/kg}$ )
2	24.59	34.865	10078	10117	2287	2296
12	24.60	34.868	10060	10098	2291	2299
36	24.14	34.899	10060	10088	2292	2298
166	18.41	34.953	10058	10069	2305	2308
252	13.39	34.343	10062	10253	2274	2318
335	10.13	34.174	10022	10262	2262	2317
385	9.14	34.143	10021	10272	2266	2323
684	5.39	34.351	10032	10224	2328	2372

## Station 13-97 21°N, 158°W 10 April 1980

4	24.97	34.722	10090	10170	2277	2296
29	24.92	34.723	10080	10170	2271	2289
136	21.90	35.028	10111	10103	2292	2291
235	16.06	34.602	10100	10214	2271	2297
345	10.40	34.162	10055	10301	2255	2310
454	7.62	34.075	10032	10306	2265	2326
748	5.06	34.379	10049	10228	2332	2374
1008	4.27	34.483	10069	10219	2356	2391